

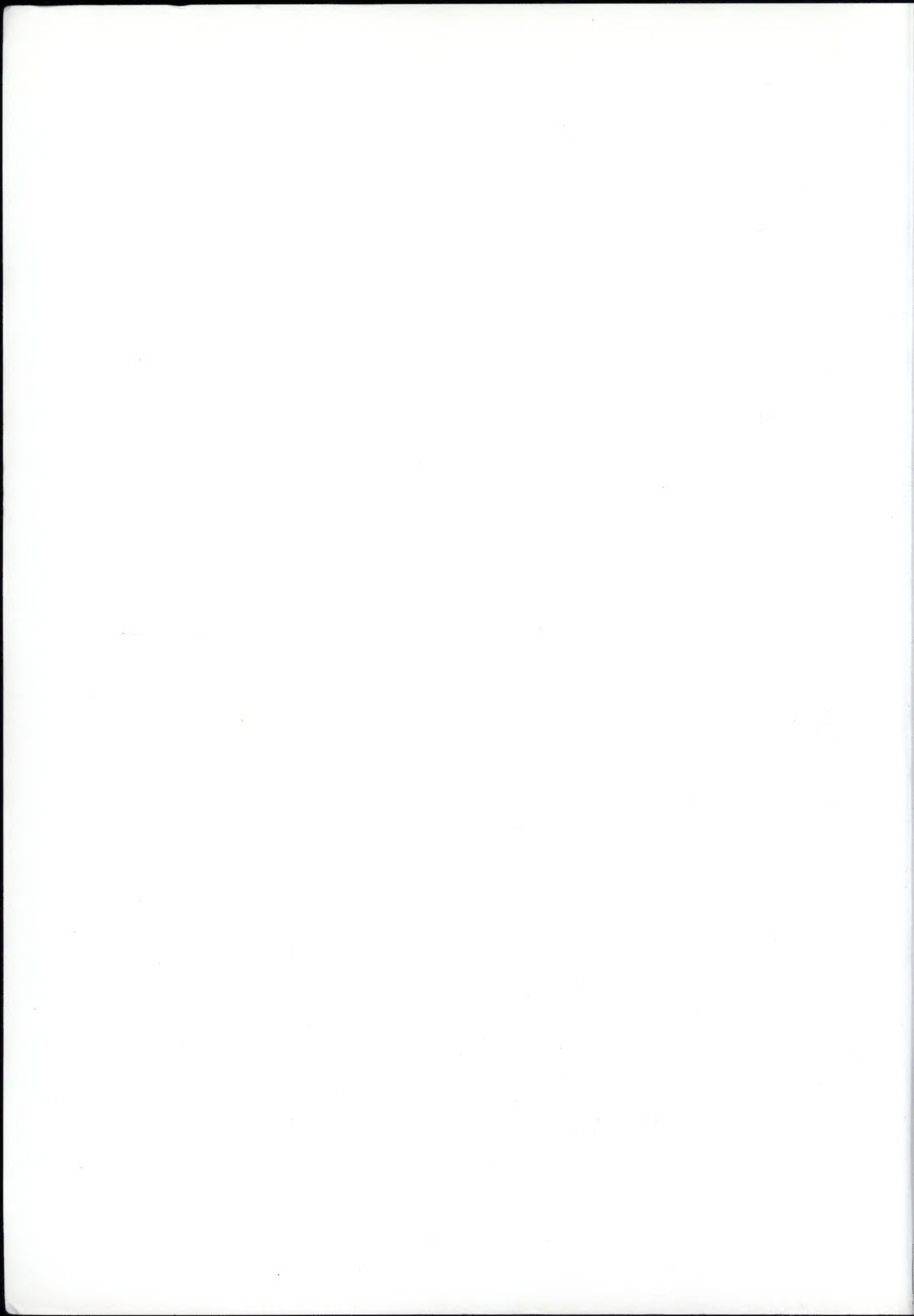
ICOM COMMITTEE FOR CONSERVATION

10th Triennial Meeting  
Washington, DC, USA  
22–27 August 1993

Preprints      Volume I



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NOTE: The following is a list of the persons who have been appointed to the various committees of the National Academy of Sciences. The names are given in alphabetical order of the last name. The names of the members of the committees are given in parentheses. The names of the members of the committees are given in parentheses.

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A NOTE ON THE COVER

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ICOM COMMITTEE FOR CONSERVATION  
Preprints 1993



## Editor's Note/Note de la rédaction

This edition of the Preprints marks the advent of a computer-based production system to replace the grid sheets that have been used in the past. While this has resulted in a more uniform and aesthetic publication, the introduction of these new procedures has held many challenges. Among these have been time constraints that have prevented a final review of text or layout by the authors. Nonetheless, I hope that they and all who consult these Preprints will be satisfied with the end result.

Another new feature of these Preprints is the inclusion of abstracts from the poster session of the 10th Triennial Meeting. The abstracts are arranged here in the order in which they appear in the poster session, rather than by Working Group.

I would like to thank the Working Group Coordinators and the authors for their co-operation and support throughout the preparation of these volumes. A special vote of thanks is due to the members of the Preprints Committee, who gave so generously of their time and energy, not only in reviewing the submissions with such diligence, but also through their assistance during the subsequent editing process. Finally, I am grateful to the editors of the poster abstracts for proposing and undertaking this complement to the Preprints.

Cette édition des prétrages marque une étape, celle de l'informatisation du système de production, accompagnée de la disparition des grilles utilisées auparavant. Si, en conséquence, l'aspect de la publication est plus uniforme et esthétique, l'introduction de ces nouvelles procédures a présenté de nombreux défis. On peut trouver à leur nombre des contraintes de temps qui n'ont pas permis aux auteurs de procéder à une révision finale des textes ou de la mise en page. J'espère toutefois que les auteurs aussi bien que tous ceux qui consulteront ces prétrages seront satisfaits du résultat final.

Une autre innovation du système est l'inclusion des résumés de la séance des panneaux d'affichage de la 10ème réunion triennale. Les résumés sont arrangés ici dans l'ordre de la séance plutôt que par groupe de travail.

Je voudrais remercier les Coordinateurs des groupes de travail ainsi que les auteurs de leur coopération et leur soutien au cours de la préparation de ces volumes. Un vote de remerciements s'adresse tout spécialement aux membres du Comité des prétrages qui ont si généreusement consacré leur temps et énergie non seulement à la révision diligente des textes qui leur étaient soumis, mais aussi au travail d'édition qui en découlait. Je voudrais enfin exprimer ma reconnaissance aux éditeurs des résumés des panneaux d'affichage pour avoir proposé et mené à bien ce complément aux prétrages.

—J.B.



ICOM COMMITTEE FOR CONSERVATION

10th Triennial Meeting  
Washington, DC, USA  
22-27 August 1993

Preprints

ICOM Committee for Conservation  
Paris 1993



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ACKNOWLEDGEMENTS

These Preprints are published jointly by the ICOM Committee for Conservation and the following organizations:

The Getty Conservation Institute, Marina del Rey, USA  
Patrimoni Artistic Nacional, Andorra la Vella, Andorra  
Direction des Musées de France, Paris, France  
Instituto de Conservación y Restauración de Bienes Culturales,  
Madrid, Spain  
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Hasenkamp Internationale Transporte, Köln, Germany

The ICOM Committee for Conservation recognizes with gratitude the above contributions which have made this publication possible.

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Published by the ICOM Committee for Conservation, 1993.  
ISBN 0-935868-65-8  
Printed in the United States of America

Available from:

Allen Press, Inc.  
1041 New Hampshire Street  
P.O. Box 368  
Lawrence, Kansas 66044  
USA  
fax (913) 843-1244

James & James (Science  
Publishers) Ltd.  
5 Castle Road  
London NW1 8PR  
United Kingdom  
fax 44 (71) 284-3737

ICCROM  
Via di San Michele 13  
00153 Rome  
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# Working Group I

Scientific Examination of Works of Art

Investigation scientifique des oeuvres d'art





## Abstract

Chinese export silver objects—bowls, teasetts, candlesticks, spoons and other tablewares, were manufactured in Chinese port cities and transported to the west by returning merchants and ships' officers, usually for personal use, in the late 18th and throughout the 19th centuries. These silver objects differ significantly in style, method of manufacture, and composition from their contemporary American and British counterparts. Energy dispersive x-ray fluorescence analysis of more than 100 Chinese export silver wares has been completed and the resulting data compared to that obtained from British and American silver objects of the same period. The data show that while silver content remained relatively constant throughout the period, gold content of Chinese export silver did vary throughout the 19th century, due probably to the source of silver metal used. This variation did not follow the pattern established by British and American silver, however. Further, Chinese silversmiths were found to have used certain marks to indicate objects of particularly fine compositional quality, although their methods of fabrication differed from those used in the west.

## Keywords

Silver, Chinese, analysis, x-ray fluorescence

## X-Ray Fluorescence Analysis of Chinese Export Silver

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## Introduction

Chinese export silver are silver objects produced in China using traditional Chinese techniques, but chiefly following Western forms, for export to the west during the period c. 1785–1885. This period was characterized by great growth of trade between the west, chiefly the United States and other English-speaking countries, and certain Chinese ports. However, Chinese export silver wares were not generally sent by the ship-load as trade goods to Western countries. Rather, they were commissioned by and purchased in the trade ports of China by Western sea captains, tradesmen and merchants for their personal use. Because the objects were not shipped to the west in vast quantity, and because they were made chiefly following Western forms and styles, it has only been within the past 25 years that this group has been recognized and studied as a unique and collectible group of silver.

Energy-dispersive x-ray fluorescence analysis has been performed on a collection of over 100 Chinese export silver objects dating from the early 19th to the early 20th centuries. XRF is an ideal analytical tool for this purpose—it is non-destructive, requiring no sampling from the object, yet can provide quantitative data for major and minor components of many alloys in an efficient fashion. While the compositional features of silver and pewter made and used in Britain and in America from the late 17th through the mid-20th centuries has been well-established (1), the compositional features of Chinese export silver have not previously been addressed. This report compares the overall compositional quality of Chinese export wares with British and American silver of the same period. Specific comparisons of Chinese export silver products from one silversmith to another or between various Chinese ports will comprise a subsequent report.

## Experimental

Quantitative energy dispersive x-ray fluorescence analysis of the bulk of the collection reported here was completed using the system described by Hanson (1,2). Instrumentation consisted of a Kevex 4000P energy dispersive x-ray spectrometer with a SiLi detector and 0.25 mm beryllium window. A pulse height analyzer (Packard 950), computer memory (Packard 901), system control (Packard 980A), and tape/type control (Packard 970) interfaced with a Hewlett-Packard 2114B computer and teletype readout. Pure silver was used as a background. Excitation was achieved using a cadmium-109 radioactive source and data collection continued until a count of 5000 on the silver K peak was reached. Although x-ray fluorescence analysis is inherently a surface analysis technique, the frequent handling and polishing of these objects over a period of at least 80 years was considered to have been sufficient to remove any elemental surface enrichment resulting from manufacturing processes. One area of each part of each object was analyzed; data were tabulated and summarized (average  $\pm$  standard deviation) for the four elements of greatest interest and those found to be most useful in previous studies—silver, copper, gold, and lead. Precision for these four elements (10 repeated analyses of the same spot) using the Winterthur silver reference standard 47.4, prepared by Handy and Harman Co., New York, N. Y., to contain 92.5% silver 7.0% copper and 0.5% gold, was found to be: Silver— $92.64 \pm 0.08$  %; Copper— $6.85 \pm 0.06$  %; Gold— $0.49 \pm 0.01$  %. Analyses reported here of two Spanish coins from Mexico or from the Mexican mint was done using a Kevex Model 8050 750 x-ray fluorescence spectrometer with a silver secondary target at 40 kV and 1.7 mA ratioed to the same silver alloy standard, 47.4, and normalized.

## Results and Discussion

### *Compositional features*

The first step in data evaluation was to establish compositional baselines using those Chinese Export objects with firm attributions, i.e., those with makers' marks which could be attributed to a specific maker working in a specific period. The dates of the objects ranged from the late eighteenth to the early twentieth century. This time span has been divided by Forbes, et al. (3) into three periods: first, a "China Trade" period from about 1785–1840, during which Chinese trade with America grew steadily; secondly, a "late China Trade" period from 1840–1885, during which the bulk of Chinese Export decorative silver wares came to the United States; and thirdly a "post-China Trade" period from 1885–1912, during which China lost to Japan her predominance in the export of many materials including silver. The chemical compositions of 48 strongly attributed hollow ware objects are summarized and arranged according to these three periods in Table I. Nine objects dated from the early period and had an average silver content of about 92%. Twelve from the middle or "Late China Trade" period averaged about 91% silver and 27 from the "Post-China Trade" period averaged about 93% silver. The average silver content of all pieces is 92.1%.

Table I. Chinese export silver. Variation of composition with time period.

Period	Date	# obj/parts		Wt. % (x ± s)				“90”
				Ag	Cu	Au	Pb	
Hollow ware								
China trade	1805–1810	9	33	91.9 ± 3.3	7.8 ± 2.8	.2 ± .1	.1 ± .1	1
Late China trade	1840–1885	12	38	90.7 ± 3.0	8.7 ± 2.9	.2 ± .1	.2 ± .1	6
Post-China trade	after 1885	27	70	92.3 ± 2.9	6.7 ± 2.9	.06 ± .05	.2 ± .1	14
Flatware								
China trade	1785–1840	20	39	89.8 ± 2.6	9.6 ± 2.5	.2 ± .1	.2 ± .1	—
Late China trade	1840–1885	26	58	86.1 ± 5.5	12.3 ± 2.3	.2 ± .1	.2 ± .1	—
Post-China trade	after 1885	41	77	92.0 ± 4.8	7.6 ± 4.8	.03 ± .03	.2 ± .1	25

Of particular note is the compositional consistency exhibited by this large group of objects over a period of more than 100 years. Such consistency with time has been previously observed in British silver where silver content has remained at or near the British sterling standard (92.5% silver) for several centuries. In this instance, compositional consistency was the result of strongly enforced regulations regarding the composition of the alloy used (4). In contrast, American silversmiths labored under no such regulations; the silver content of their products, although averaging around 90% silver, actually varied over a wide range (5).

The compositional consistency of Chinese export objects has two possible explanations. The first is that Chinese silversmiths were regulated, either by law or self-imposed standards, to produce wares of a certain compositional quality. A 1915 Canton Directory states that among the 72 guilds which controlled the economic life of the vicinity, the Goldsmith's Guild ranked second only to the Bankers' Guild and probably had a similar prominent position during the China trade period (6). Whether one of the functions of this guild was to regulate the



compositional quality of silver produced is not yet known. A second explanation for the compositional consistency of Chinese export silver is that the raw materials to which the Chinese silversmiths had access were compositionally consistent. This point-of-view is supported by the statement that "so-called 'chopped' dollars (i.e., silver coins which entered Canton and other ports as payment for trade items) were probably the most important source of silver" for the manufacture of Chinese silver (7). By 1854, the United States alone had shipped to China in excess of 108 million dollars (8). Analysis of American silver coins of that period show them to contain on the average, about 90% silver (9) which corresponds well to the average of 48 marked and dated Chinese hollow ware objects in Table I.

Although silver content is consistent over the period covered by Chinese export objects, gold content is not. The presence of trace amounts of lead and gold in silver objects has been used as an indication of relative age in British and American silver objects. Those objects which postdate the mid-19th century generally contain little or no gold or lead, while those from earlier periods do. In addition, a rough correlation can be made between amount of gold and the approximate date of the object, with those pieces containing higher gold concentrations being of early manufacture (10).

The gold content of this group of 48 Chinese export pieces does not follow the pattern established by British and American objects. Gold content for the 9 objects dating from the China Trade period averages 0.2%, a high value when compared to American and British objects of the same period. The twelve Chinese export objects from the Late China Trade period also have an average gold content of about 0.2%, *much* higher than that found in British and American silver of the same period and more typical of early to mid-18th century British and American silver. The gold content of 27 Post-China trade period drops to an average of 0.1%. American and British silver of this late period contain virtually no gold.

It appears that Chinese silversmiths relied on some source in addition to British and American silver coins for their raw materials, since these would have had a much lower gold content. One additional source of material was "old" American silver sent to China to be refashioned into a new style or form. There is, in fact, documentary evidence of the remaking of old American silver brought to China by sea captains expressly for that purpose (11). And if this "old" silver had been made in the 18th C., then it could well have contained the high concentrations of gold found in Chinese silver of the late China Trade period. Other possible sources of silver with a relatively high gold content are silver refined from Chinese ores or silver from the Spanish trade with China via the Philippines. A group of 42 Spanish silver coins dating from about 1750 to 1842 was found to contain 94% silver and 0.07% gold (12). Recent XRF analysis of a 1743 Spanish dollar minted in Mexico and a Spanish silver "2-bit" piece averaged 95.3% silver and 0.06% gold (13).

Data obtained from well-authenticated Chinese export flatware show a similar compositional pattern. Twenty flatware objects dating from the Late China Trade period contained an average of 0.2% gold, but 41 from the Post-China Trade period contained an average of only 0.03% gold. The lower average silver content of the flatware from the late China Trade period, 86%, should not necessarily be construed to mean that flatware was made using a lower quality silver alloy than hollow ware in this period. Actually, 24 of the 26 pieces tested in this group were from one particular hollow-handled set, all presumably made at one time and apparently from a particularly low-silver containing batch of metal. If that set is excluded from the calculation, the average silver content of the remaining 2 objects is about 90% silver. The silver content of the Post-China Trade flatware is higher, about 92%, and reflects the use of a higher quality silver denoted by the figure "90" stamped on 25 of the 41 pieces.

Many Chinese export silver objects are marked with numbers in addition to makers' initials, name, or Chinese ideographs. The most frequently used number is "90" which appeared on 20 hollow ware objects. It was theorized that Chinese silversmiths may have used this mark either to indicate that the alloy used

contained 90% silver or that objects so marked were made of a particularly fine alloy (high silver content) although not necessarily 90%. Analysis of these 20 pieces and comparison of the data obtained from 25 other pieces which bore a makers' mark but no "90" mark showed there is indeed a compositional difference between the two groups (see Table II). The "90" marked hollow ware averaged about 94% silver while the non-"90" group averaged less than 91% silver. Obviously, Chinese silversmiths attached some significance to the use of the "90" mark and used it to denote objects of particular value or compositional quality. They could not have known the exact composition of the alloys used but would certainly have recognized the relative differences in silver content by differences in color and workability.

Table II. Chinese export silver. Composition of objects marked "90".

Mark	# obj/parts		Wt. % ( $\bar{x} \pm s$ )			
			Ag	Cu	Au	Pb
Hollow ware						
"90"	20	52	94.0 $\pm$ 1.8	5.7 $\pm$ 1.8	.04 $\pm$ .02	.2 $\pm$ .1
No "90"	25	81	90.8 $\pm$ 3.0	8.7 $\pm$ 2.9	.2 $\pm$ .1	.2 $\pm$ .1
Flatware						
"90"	25	49	95.3 $\pm$ 0.5	4.2 $\pm$ 0.4	.02 $\pm$ .01	.2 $\pm$ .1
No "90"	48	104	87.3 $\pm$ 2.9	12.1 $\pm$ 2.8	.02 $\pm$ .01	.2 $\pm$ .1

All 25 pieces in one set.

The use of quality marks was common in 19th century American silver. Such words as COIN, PURE COIN, STERLING, PREMIUM, etc., frequently appeared, although analysis has shown that in many cases these words were used more as advertising and in attempts to fool the unwary public than as actual indications of compositional quality (14). Numerical quality marks such as 10.15 and 11 (oz./Troy pound) were used by silversmiths in Baltimore (15) between 1815 and 1865, but no American examples of a "90" mark have been found. Presumably, Chinese silversmiths using this mark were trying to convey the same kind of compositional quality as those American makers who used the words COIN and PURE COIN, since American coinage of the period contained about 90% silver. However, the Chinese products contained considerably more silver than 90%, averaging about 94%.

Flatware marked with the "90" mark had an even higher silver content, about 95%. However, since the 25 pieces tested were all from one particular large set, one must be cautious in concluding that the silver content of all "90" marked flatware would be as high. The silver content of 48 non-"90" marked silver flatware objects averaged only 87% silver.

Other marks stamped on silver objects may also have been intended to convey an actual or implied degree of compositional quality. Thirteen objects bearing only uninterpreted Chinese ideographs averaged 93.0% silver. Two objects bearing pseudo-hallmarks, that is, marks copied from hallmarks placed by British silversmiths to denote the name of the maker, the city, the year made, the quality (sterling), and payment of duty, contained 90.1% silver.

#### *Compositional Variations with Provenance*

Canton was the only port in China to which English and Americans were permitted until 1842 and 1843 when four additional Treaty Ports were opened (16). As a result, Chinese silver made for export was produced in only a few cities. A comparison of those objects made in Canton with those from Hong Kong and Shanghai is given in Table III. The data suggest that Hong Kong-made objects are of significantly higher silver content than those made in the other two cities. Actually, this apparent high silver content really reflects the fact that all 11 of these objects bear the "90" mark. The five Shanghai made objects, none of which are "90" marked, averaged 92% silver while 19 Canton made objects averaged about 91% silver. Silver objects from all three ports are



Table III. Chinese export silver. Variation of composition with provenance.

Port	Makers represented	# obj/parts		Wt. % ( $\bar{x} \pm s$ )				"90"
				Ag	Cu	Au	Pb	
Hong Kong	IW, WH/WM c. 1850-1890	11	27	94.1 $\pm$ 1.6	5.5 $\pm$ 1.5	.05 $\pm$ .02	.2 $\pm$ .1	All
Shanghai	LW, TC, HC c. 1885-1890	5	13	91.8 $\pm$ 3.7	7.9 $\pm$ 3.5	.04 $\pm$ .02	.2 $\pm$ .1	None
Canton	CS, SS, ACAO/ AEAO	19	64	91.0 $\pm$ 2.9	8.5 $\pm$ 2.8	.2 $\pm$ .1	.2 $\pm$ .1	None
	CU/k, CUT, E, Pd, YS	4	12	91.7 $\pm$ 3.6	7.8 $\pm$ 3.39	.1 $\pm$ .1	.2 $\pm$ .1	All
	W, KHC c. 1800-1870	15	52	90.8 $\pm$ 2.7	8.6 $\pm$ 2.6	.2 $\pm$ .1	.2 $\pm$ .1	None

thus quite uniform in composition and high in silver content, confirming initial findings as outlined in Table 1.

*Fabrication Techniques*

While Chinese silversmiths used many of the same manufacturing techniques—raising, casting, soldering—used by their western counterparts, certain distinctions were noted. Raised objects are sometimes made of extremely thick metal with the additional joining of many separate parts. Unusual “scarf” solder joints were used to attach the thick end of a handle to the shank of a spoon or fork (17). This process is seen in a demitasse spoon bearing a shell decoration on the handle. Close visual examination reveals the presence of a chevron or “V” shaped seam beneath the shell indicating a joint between the shell and the handle. The shell end was cast in two parts and then soldered together before being attached to the handle. A third seam can be seen across the narrow mid-portion of the handle. At this point, the broad handle end was attached to the rest of the spoon by an off-set scarf joint rather than the western butted solder joint. The small spoon thus consists of 4 separate cast parts.

*A Compositional Anomaly*

During the examination and analysis of any large group of objects, there are often a few which are not what they first appear to be. Such objects may have been repaired, altered, or added to in the course of their lives or may simply be reproduction objects. One particularly anomalous object in this collection of Chinese export silver is an eggstand, complete with six cups and six spoons. The stand and spoons are marked with the date letter E, whose use is attributed to a silversmith working in Canton in the second quarter of the 19th century. The egg cups are unmarked.

Five parts of the stand were analyzed and averaged about 94% silver (Table IV). Gold and lead content were typical of other mid 19th c. Chinese export silver. Four of the six spoons were analyzed and found to contain only about 89% silver. Analysis of the cups, however, showed them to contain anywhere from 35 to 93% silver as well as large amounts of copper, zinc and nickel. The variation in apparent silver content as well as the presence of two additional

Table IV. Chinese export silver. XRF analysis of eggstand, spoons and cups. Date Letter E, Canton, 1825-50.

Part	# parts	Wt. % ( $\bar{x} \pm s$ )					
		Ag	Cu	Au	Pb	Zn	Ni
Stand	5	93.8 $\pm$ 1.4	5.6 $\pm$ 1.3	.2 $\pm$ .03	.1 $\pm$ .05	.1 $\pm$ .1	0
Spoons	5	89.2 $\pm$ 0.8	10.1 $\pm$ 0.8	.2 $\pm$ .04	.2 $\pm$ .04	0	0
Cups	12	71.4 $\pm$ 15.7	16.9 $\pm$ 9.9	.1 $\pm$ .04	.4 $\pm$ .1	7.7 $\pm$ 3.9	3.0 $\pm$ 2.3
Cups (corrected for silver plating)	12	—	61.0 $\pm$ 1.3	—	—	30.0 $\pm$ 2.5	9.5 $\pm$ 2.5

elements, nickel and zinc, suggested that the egg cups were not a silver alloy but actually silver-plated paktong. The exclusion of silver from the calculation of composition revealed that copper, nickel, and zinc were present in the ratio expected from previous analyses of paktong (18), confirming that the cups had been silverplated. It thus appears that the cups were probably not original to the eggstand and were made to replace earlier lost cups.

### Conclusion

This analytical study of Chinese export silver has revealed new information about the procedures and alloys used by Chinese silversmiths throughout the 19th century and has established the compositional characteristics of a third group of regional silver. Chinese silversmiths of the 19th century were excellent craftsmen who were well aware of the differences in compositional quality of their alloys and maintained the silver content of their products at about the 90% level over a period of more than 100 years and in several different ports. Although their work was influenced stylistically by the demands of their Western customers, they continued to use traditional Chinese techniques of fabrication, reflecting the Chinese labor intensive culture where workers were plentiful and tradition important.

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## Résumé

Cette étude porte sur la technique de polychromie de quatre boîtes funéraires en bois, datées du VII<sup>e</sup> siècle de notre ère qui furent découvertes en Chine. Après une description de la polychromie de chaque boîte, les résultats d'analyse des différents types de pigments et de liants utilisés sont exposés. Les moyens mis en oeuvre pour cette étude sont l'observation binoculaire, les examens photographiques, la réflectographie IR et la microscopie électronique à balayage. Les identifications de matériaux sont effectuées par microchimie, microanalyse X, fluorescence X, diffraction X, spectrométrie IRTF et chromatographie en phase gazeuse. Deux techniques différentes de décor utilisant un nombre limité de pigments et la présence d'enduits recouvrant l'intérieur de chaque boîte ont pu être mis en évidence.

## Mots clefs

Boîte, Chine, pigment, liant, examen photographique, analyse microchimique, analyse élémentaire, Pelliot

## Etude scientifique du décor de quatre boîtes funéraires en bois provenant de Chine

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## Introduction

Quatre boîtes funéraires en bois, *boîte aux musiciens masqués*, *boîte à décor végétal stylisé*, *boîte aux amours musiciens* et *boîte aux oiseaux*, sont exposées au musée Guimet à Paris. Elles ont été rapportées de Chine par la mission Paul Pelliot après leur découverte en 1907, au cours de fouilles entreprises sur le site d'un temple bouddhique situé à Soubachi sur les rives de la rivière de Koutcha, province du Xinjiang (Sinkiang). Des pièces de monnaie de la période *wou-tchou*, retrouvées à l'intérieur de la *boîte aux oiseaux* avec des ossements, un petit sachet renfermant des dents et des fragments de feuilles d'or, permettent de supposer que ces boîtes datent au plus tard du milieu du VII<sup>e</sup> siècle [1].

Il s'agit de boîtes rondes dont le corps a été obtenu en évidant une pièce de bois, au tour. Leur couvercle, légèrement conique, rappelle la forme de certains chapeaux asiatiques. L'extérieur de chaque boîte est décoré de motifs différents alors que l'intérieur n'est recouvert que d'un enduit blanc ou coloré [2]. L'état de conservation de la polychromie externe est variable d'une oeuvre à l'autre. Il résulte du contexte d'enfouissement: la *boîte aux amours musiciens*, qui était enveloppée dans une peau d'animal, est de ce fait la mieux conservée. D'autres boîtes reliquaires, aux formes identiques, sont conservées dans des musées étrangers mais, à notre connaissance, aucune étude scientifique sur leur polychromie n'a été publiée.

La *boîte aux musiciens masqués* et la *boîte à décor végétal stylisé* ont subi, en 1959, une série d'examens photographiques et radiographiques [3]. En 1991, dans le cadre d'une recherche sur les objets provenant de la mission Pelliot, une étude plus approfondie de ces boîtes, avec analyse de leur polychromie et de l'enduit intérieur est entreprise et étendue aux deux autres boîtes: la *boîte aux amours musiciens* et la *boîte aux oiseaux*.

## Techniques mises en oeuvre

Des examens photographiques [4] et de nombreuses observations sous loupe binoculaire ont été effectués. Ils ont permis de choisir les emplacements de microprélèvements pour les études stratigraphiques menées sur coupes à l'aide de la microscopie électronique à balayage [5]. Des analyses élémentaires par microfluorescence X directe de la surface des boîtes complètent ces premiers résultats. La diffraction de rayons X permet l'identification des préparations et des enduits intérieurs. Les liants ont été identifiés par des tests microchimiques [6] et les vernis, par spectrométrie infrarouge à transformée de Fourier et par chromatographie en phase gazeuse [7].

## Description:

La *boîte aux musiciens masqués* (voir Fig. 1)

(Inv.: MG 17697. Hauteur totale: 0,24 m. Diamètre: 0,34 m. Bois: peuplier)

La polychromie de cette boîte, la plus abîmée parmi celles étudiées, se distingue des autres par son décor appliqué sur une préparation blanche laissée en réserve.

Ce décor est peu lisible surtout sur le couvercle qui présente deux profondes fissures et de nombreuses griffures (voir Fig. 2). Les photographies infrarouges, réalisées en 1959 au LRMF et un nouvel examen en réflectographie infrarouge restituent une partie des tracés partiellement disparus. Sur le couvercle, subsiste

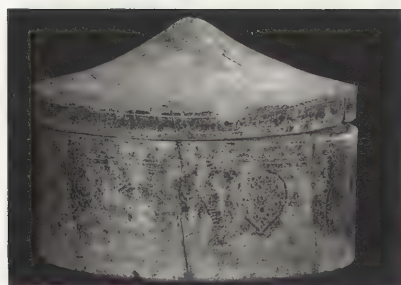


Fig. 1: Boîte aux musiciens masqués.

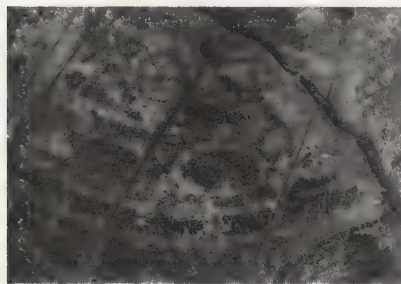


Fig. 2: Détail du couvercle: décor de cabochons et de perles sur une préparation blanche laissée en réserve. Fentes et nombreuses griffures.

\* Auteur à qui la correspondance devrait être adressée.





Fig. 3: Détail de la ceinture de la boîte : motif végétal entouré de personnages.

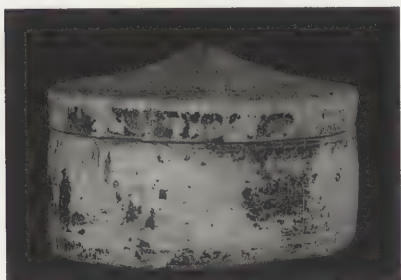


Fig. 4: Boîte à décor végétal stylisé.

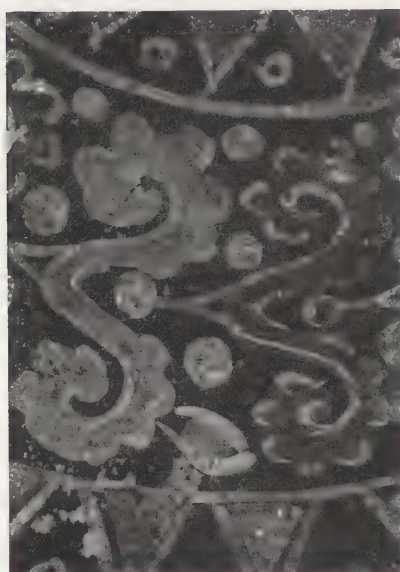


Fig. 5: Détail, motifs stylisés représentant des calices de fleurs entre des frises de triangles, dits décor en lambrequin.



Fig. 6: Boîte aux amours musiciens.

la trace de quatre médaillons avec des personnages. Entre les médaillons venaient s'insérer des oiseaux. Des frises de triangles et de cabochons ovales séparés par des pastilles blanches imitant des perles complètent ce décor, au centre du couvercle et sur le bord. Sur la ceinture, mieux conservée, les mêmes frises sont observées. Elles encadrent une série de quatre médaillons avec des personnages. Des motifs végétaux s'intercalent entre les médaillons (voir Fig. 3).

Les couleurs ont en partie disparu. Toutefois, il existe une dominante brun rouge, probablement due à la présence d'une laque ou d'un vernis altéré. Des pigments noirs et des traces bleues sont visibles sur la ceinture de la boîte.

L'intérieur de la boîte a un aspect de surface hétérogène, de couleur violacée et grisâtre, vestige, peut-être, de son contenu et d'un enduit recouvrant le bois comme sur les autres boîtes. La trop grande hétérogénéité de la matière imprégnant le support nous a empêché de faire des prélèvements pour son identification.

#### *La boîte à décor végétal stylisé (voir Fig. 4)*

(Inv: EO 1093. Hauteur totale: 0,135 m. Diamètre: 0,205 m. Bois: Saule.)

Sur la ceinture de la boîte, d'aspect blanchâtre, la polychromie a en grande partie disparu; seuls quelques îlots colorés sont encore visibles. En revanche, sur le couvercle, elle est mieux conservée et reste lisible malgré quelques grandes lacunes et des soulèvements (voir Fig. 5). Le fond noir est décoré de motifs végétaux stylisés ocre et marron verdâtre, cernés de traits clairs et représentant des calices de fleurs. Des frises de triangles, appelées décor en lambrequin, bordent ces motifs [8]. Des boutons floraux stylisés sont dessinés au centre du couvercle. Un vernis brun rouge dans lequel s'intègrent des zones plus rouges, glaciés de laque probablement, recouvre l'ensemble de la polychromie. Il est difficile de distinguer ces deux matières même sur les coupes stratigraphiques. La surface, terne et altérée, ne permet pas de discerner de façon plus précise les différentes nuances de la polychromie.

L'intérieur de la boîte est recouvert d'un enduit ocre dont l'aspect de surface n'est pas homogène.

#### *La boîte aux amours musiciens (voir Fig. 6)*

(Inv: EO 1094. Hauteur totale: 0,164 m. Diamètre: 0,235 m. Bois: peuplier.)

La polychromie de cette boîte est celle qui est la mieux conservée. Seuls quelques soulèvements sur le couvercle et quelques lacunes sont visibles. Des motifs verts et jaunes sont peints sur un fond rouge. Sur le couvercle, six enfants nus sont inscrits dans six médaillons bordés de triangles entre des doubles cercles (voir Fig. 7). Au centre, une fleur à huit pétales a été représentée dans un médaillon délimité par le même motif. Six oiseaux prennent place dans les espaces entre les médaillons. Une bordure de triangles semblable à celle des médaillons décore le bord du couvercle. Sur la retombée, un motif de fleurs et de petites feuilles jaunes vient achever le décor. Sur la ceinture de la boîte, on retrouve les motifs triangulaires, décor en lambrequin, encadrant des rinceaux de feuilles vertes cernées de traits jaunes. Un vernis recouvre la matière picturale. Sous lumière ultraviolette, il présente une vive fluorescence orangée qui met en évidence la direction des coups de la brosse qui a servi à son application. Les lacunes apparaissent en noir.

L'intérieur de la boîte est tapissé d'une matière beige.

#### *La boîte aux oiseaux (voir Fig. 8)*

(Inv: EO 1092. Hauteur totale: 0,215 m. Diamètre: 0,205 m. Bois.)

Comme pour la *boîte aux amours musiciens*, la polychromie est assez bien conservée à l'exception de la base où une partie de la matière picturale a disparu. Le décor se lit facilement malgré, par endroit, la présence de dépôts grisâtres. Sur le couvercle, le décor est composé de cinq médaillons à motifs noirs et jaunes sur fond rouge entourés de triangles. Au centre, des oiseaux stylisés, probablement des pigeons, ont été peints. Chaque médaillon est séparé par un motif floral à trois pétales (voir Fig. 9). Sur la retombée du couvercle, on observe un décor de fleurs. Des rinceaux végétaux et des motifs géométriques entourent le corps de



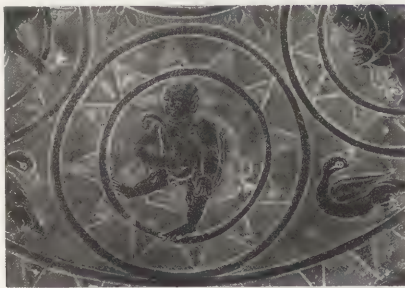


Fig. 7: Détail sur le couvercle, enfant nu dans un médaillon entouré d'un décor en lambrequin et oiseaux.



Fig. 8: Boîte aux oiseaux.



Fig. 9: Détail du couvercle avec des dépôts grisâtres résultant de l'altération des feuilles d'étain qui étaient appliquées sur les triangles des décor en lambrequin.

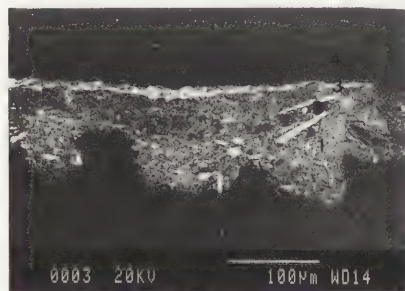


Fig. 10: Image en électrons rétrodiffusés au microscope électronique à balayage : 1—préparation, 2—fond, 3—tracé à l'orpiment, 4—épais vernis.

la boîte. Un vernis recouvre l'ensemble de la polychromie. Sous lumière ultraviolette, il présente une vive fluorescence qui révèle sa direction d'application. Les lacunes ainsi que des dépôts gris répartis de façon inégale à la surface de la boîte sont visualisées en sombre.

Une matière ocre rouge recouvre l'intérieur de la boîte.

### Résultats d'analyse

#### Les préparations:

L'extérieur de chaque boîte est recouvert d'une préparation de couleur et de composition minérale différentes. En revanche, le liant, semblable dans toutes les préparations, est une colle protéinique.

Pour la *boîte aux musiciens masqués*, il s'agit d'une préparation blanche au gypse et pour la *boîte à décor végétal stylisé*, d'une préparation grisâtre à base d'argiles (illite et kaolinite) et de quartz. Sur les deux autres objets, les préparations sont colorées: orange, obtenu par mélange d'ocre avec du gypse et de la bassanite pour la *boîte aux amours*, et rose à base de gypse coloré par une laque organique rouge pour la *boîte aux oiseaux*.

#### Réalisation des motifs décoratifs:

##### Couche de fond:

A l'exception de la *boîte aux musiciens masqués*, pour laquelle le décor est appliqué directement sur la préparation laissée en réserve, les *boîtes à décor végétal*, *aux amours musiciens* et *aux oiseaux* ont été recouvertes d'une couche colorée jouant le rôle de fond avant le tracé des motifs décoratifs. Sur la *boîte à décor végétal*, il est composé de noir de carbone. Sur la *boîte aux amours musiciens*, le fond est rouge. Il correspond à la matière rose vif, visible dans les lacunes et qui, recouverte de vernis, prend un aspect laqué rouge soutenu. Cette matière de fond est composée d'une laque organique rouge additionnée d'une charge minérale de même nature que la préparation sur laquelle elle repose, et d'un liant protéinique (voir Fig. 10). Le fond de la *boîte aux oiseaux* est également rouge mais, dans ce cas, c'est une fine couche de laque rouge dont l'épaisseur varie entre 5 et 10 microns.

##### Décor:

La *boîte aux amours musiciens* et la *boîte aux oiseaux* sont à rapprocher par le nombre restreint de couleurs et la nature des matériaux employés dans la réalisation des éléments de décor exécutés.

Sur la *boîte aux amours musiciens*, de l'orpiment est identifié dans le tracé jaune des petites feuilles et des cernes. Mêlé à de l'indigo [9], il entre dans la composition de la couleur verdâtre des personnages, du tour des médaillons et des feuillages de la ceinture de la boîte. De la feuille d'étain est décelée à l'intérieur des décors en lambrequins.

Pour la *boîte aux oiseaux*, les mêmes pigments sont présents dans les tracés. L'aspect noir observé pour les oiseaux, les motifs floraux et les feuilles de la ceinture de la boîte est obtenu avec l'indigo, utilisé pur. Les éléments de décor réalisés avec ce pigment deviennent invisibles en reflectographie infrarouge. L'observation sous loupe binoculaire des motifs en lambrequin et des pétales, complétée par l'analyse, révèlent, comme sur la *boîte aux amours musiciens*, la présence de feuilles d'étain très usées dont l'emplacement apparaît brun sous lumière ultraviolette. Ces feuilles ont presque totalement disparu, laissant voir la matière rose du fond. L'altération de ces décors métalliques est à l'origine des dépôts grisâtres qui sont visibles à la surface de la polychromie.

Le décor de la *boîte à décor végétal*, est plus élaboré. En plus de l'orpiment, de l'indigo et des feuilles d'étain, sont utilisés une laque brun rouge, une terre argileuse de même nature que la préparation et du blanc de plomb. Ce dernier pigment apparaît sur le cliché radiographique avec une opacité importante et correspond au tracé de la frise de triangles du bord du couvercle et des contours



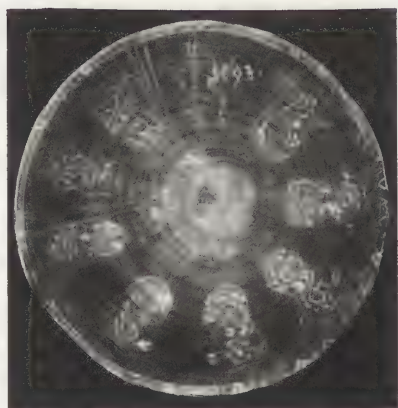


Fig. 11: Radiographie du couvercle de la boîte à décor végétal montrant principalement les motifs de calices à intérieur ocre rouge.

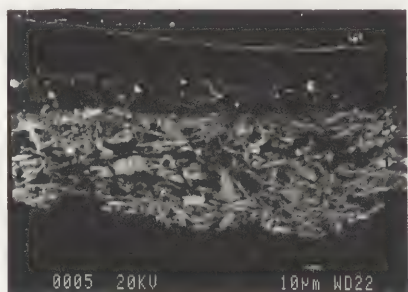


Fig. 12: Image en électrons rétrodiffusés au microscopie électronique à balayage d'une coupe stratigraphique du décor de la boîte à décor végétal stylisé 1—préparation, 2—fond noir, 3—intérieur ocre rouge, 4—vernis, 5—encrassement.

des calices de fleurs à intérieur ocre rouge (voir Fig. 11). Il peut être additionné d'une quantité variable d'orpiment. Sur l'image radiographique, on remarque également des traits qui ne sont visibles ni à l'œil nu, ni sous loupe binoculaire, ni en réflectographie infrarouge. Il pourrait s'agir d'un dessin sous-jacent à la couche picturale.

La laque brun rouge mêlée à un peu de blanc de plomb et d'orpiment constitue l'intérieur des calices ocre rouge (voir Fig. 12). L'observation de la coupe, sous lumière ultraviolette, montre que cette laque a une fluorescence comparable à celle du vernis qui la recouvre. La couleur brun rouge actuelle est probablement le résultat du vieillissement de la laque et du vernis.

L'intérieur brun verdâtre des motifs de calice de fleur est dû à l'emploi d'indigo recouvert par le vernis. Les contours clairs de ces motifs ne sont pas observés sur le cliché radiographique car ils sont réalisés avec une terre argileuse peu opaque aux rayons X par rapport au blanc de plomb. Ceci explique que, sur l'image radiographique, seul un motif de calice de fleur sur deux est visible. Il en est de même du décor en lambrequin proche du centre du couvercle.

Les feuilles d'étain sont localisées, dans ce cas, sur les boutons floraux du centre du couvercle et sur les motifs en lambrequin. L'altération de la surface a uniformisé l'aspect des couleurs. En particulier, il a fait perdre le chatoyement original de ces feuilles métalliques recherché initialement par le peintre. Ces feuilles d'étain se fondent aujourd'hui, avec les autres couleurs. Elles sont recouvertes par un vernis brun rouge ou par un glacis de laque rouge.

Pour la boîte aux musiciens masqués, malgré son mauvais état de conservation, l'étude stratigraphique apporte quelques informations sur les constituants du décor. Les perles en relief, que l'on peut observer de part et d'autre des cabochons, sont de même composition que la préparation. Les motifs dessinés en réserve sont principalement constitués d'une laque organique brun rouge et d'un noir de carbone. Des traces de bleu, indigo probablement, associé à du gypse, sont visibles sur la ceinture de la boîte. Aucune feuille métallique n'est décelée sur cette boîte.

#### Vernis:

A l'exception de la boîte aux musiciens masqués, les décors de trois autres boîtes sont recouverts d'une couche de vernis. Sur la boîte à décor végétal, le vieillissement du vernis uniformise les couleurs et rend difficile la différenciation entre ce vernis et l'emploi d'un glacis de laque organique rouge. Sur les deux boîtes les mieux conservées, boîte aux amours musiciens et boîte aux oiseaux [10], le vernis a gardé sa transparence et donne à la matière picturale tout son éclat. Les analyses préliminaires sur les vernis de ces trois dernières boîtes mettent en évidence l'utilisation de vernis à base de résine naturelle sans qu'il soit possible actuellement d'apporter plus de précision [11].

#### Enduit intérieur:

Seuls les enduits des boîtes à décor végétal, aux amours musiciens et aux oiseaux ont pu être analysés: l'enduit intérieur ocre rouge de la boîte à décor végétal est principalement constitué d'hématite et de quartz. Pour la boîte aux amours musiciens, c'est un mélange de gypse, d'argiles (illite, kaolinite) et de quartz. Cet enduit est recouvert d'une couche beige, renfermant les mêmes constituants avec, en plus, un peu d'orpiment qui la colore en jaune. Quant à la boîte aux oiseaux, il s'agit d'hématite et de goethite. La cohésion des trois enduits est assurée par un liant protéinique.

#### Conclusion

Cette étude met en évidence deux techniques de décor réalisé avec un nombre limité de pigments et des liants protéiniques. Pour une seule boîte, la boîte aux musiciens masqués, la matière picturale est appliquée directement, sans couche de fond, sur la préparation laissée en réserve, avec un nombre restreint de couleurs et sans décor métallique. Dans ce cas, un noir organique, une laque brun rouge et un pigment bleu organique, indigo probablement, sont employés. Le mauvais



état de conservation de cette boîte ne permet pas d'apporter plus d'information sur les constituants de la polychromie. Les trois autres boîtes ont pour point commun le même concept de réalisation de la polychromie malgré quelques différences dans la nature des matériaux utilisés. L'extérieur de chaque boîte est enduit d'une préparation blanche ou colorée qui est masquée par une couche de fond, noir pour la *boîte à décor végétal stylisé* et rouge pour les deux autres. Ensuite, le décor est tracé puis couvert d'un vernis qui joue un rôle important dans le rendu final des couleurs.

Sur la *boîte aux amours musiciens* et la *boîte aux oiseaux*, le décor est composé d'orpiment, d'indigo et d'une laque rouge. Des feuilles métalliques le rehaussent. Les mêmes constituants sont présents sur la *boîte à décor végétal* mais elle se distingue des deux autres par l'application, sur un fond noir, d'un tracé renfermant également du blanc de plomb et une terre argileuse. Les matériaux identifiés dans cette étude font partie de ceux généralement rencontrés sur des peintures asiatiques. Actuellement, nous n'avons, en notre possession, aucun élément d'analyse comparative sur les boîtes funéraires chinoises de même époque conservées dans les musées étrangers. Seuls, deux objets en bois sont à rapprocher des boîtes de Soubachi par leur technique de polychromie mais ils sont datés du XII<sup>e</sup> siècle. Il s'agit de deux couvertures d'un manuscrit bouddhique, conservées au musée Guimet, les mêmes pigments recouverts d'un vernis sont mis en évidence [12].

Nous espérons que ce travail encouragera des études analogues permettant de mieux connaître la technique de fabrication de ces objets.

### Remerciements

A Dominique Bagault qui a réalisé les documents photographiques. A Anne Bouquillon et Elisabeth Martin qui ont su conseiller et encourager ce travail.

Tableau récapitulatif des résultats

	Boîte aux musiciens masqués MG 17697	Boîte à décor végétal EO 1093	Boîte aux amours musiciens EO 1093	Boîte aux oiseaux EO 1092
Préparation (diffraction X)	gypse liant protéinique	illite, kaolinite, quartz liant protéinique	ocre, gypse, bassanite liant protéinique	gypse, laque rouge liant protéinique
Couche de fond (MEB)	-, préparation laissée en réserve	noir organique	ocre, CaSO <sub>4</sub> laque rouge	laque rouge
Décor (MEB)				
Orpiment	-	+	+	+
Indigo	trace	+	+	+
Noir organique	+	+	+	+
Laque organique	+	+	+	+
Blanc de plomb	-	+	-	-
Terre	-	+	-	-
Feuille d'étain	-, (mfx)	+, (mfx)	+, (MEB)	+, (mfx)
Vernis	non observé	résine naturelle IR, CPG	résine naturelle CPG	résine naturelle CPG
Enduit intérieur (diffraction X)	+, très hétérogène, non analysé	hématite, quartz, liant protéinique	gypse, illite, quartz, liant protéinique avec en surface de l'orpiment mêlé aux mêmes composés	hématite, goethite, liant protéinique

MEB = analyse élémentaire par sélection d'énergie de rayons x avec un système couplé à un microscope électronique à balayage, effectuée sur coupe stratigraphique. mfx = microfluorescence x directe à la surface des oeuvres. IR = spectrométrie infrarouge. CPG = chromatographie en phase gazeuse. - = non employé. + = présent.

### Notes et références

1. T. Akiyama, "The three wooden caskets from Subachi in the Kucha region, brought back by the Pelliot Mission", *The Bijutsu Kenkyu, the journal of art studies* (Tokyo 1957), 2-3, 266-286.  
R. Jéra-Bezard, "Une peinture murale d'un sanctuaire bouddhique d'Asie centrale." *Revue du Louvre et des musées de France* (Paris, 1983), 38-44.

- S. Gaulier, "Les boîte funéraires de Soubachi", *Douldour-âgour et Soubachi, Mission Paul Pelliot*, Edition Recherche sur les civilisations (Paris 1982), 51, 331-347.
2. cf. note 1, S. Gaulier, op.cit. 401-403. Remarquons que dans le travail de S. Gaulier, *la boîte à décor végétal* et *la boîte aux musiciens masqués* sont décrites comme n'étant pas enduites à l'intérieur.
  3. M. Hours, "Examen au laboratoire: Boîtes en bois de Subachi", *Bulletin du laboratoire de recherche des musées de France* (Paris 1959), 37.
  4. Il s'agit de photographies infrarouges et sous lumière ultraviolette ainsi que d'examens en réflectographie infrarouge. Documents photographiques réalisés par Dominique Bagault.
  5. L'appareillage utilisé est un système de microanalyse par sélection d'énergie des rayons X (Ortec système 5000), couplé à un microscope électronique à balayage JEOL JSM 840.  
 La fluorescence X est effectuée directement sur les objets. Un tube à anticathode de molybdène est utilisé, associé à un détecteur à semi-conducteur (Si-Li) et une chaîne d'acquisition de spectres.  
 La technique en chambre de Debeye Scherrer a été choisie pour la diffraction de rayons X.
  6. E. Martin, "Application des tests sur coupes minces à l'identification des émulsions dans les liants de peinture", *Annales du laboratoire de recherche des musées de France* (1977), 23-29.
  7. Spectromètre IRTF Perkin Elmer 7500, vernis extrait au chloroforme avant pastillage avec du bromure de potassium. Chromatographie en phase gazeuse sur colonne Chrompack CP Sil-5CB, longueur: 1,5 m, diamètre intérieur: 0,25 mm. Injecteur: 300°C, détecteur: 330°C. Recherches des corps gras après estérification avec BF3-butanol, programmation de température: 80°C à 230°C, 5°C/mn. Recherche de cire et de résine après extraction au chloroforme, programmation de température: 120°C à 330°C, 10°C/mn.
  8. cf. note 1, S.Gaulier, op. cit. p 333: " Les triangles alignés en dents de scie qui forment un décor de bordure constituent un des éléments favoris de l'école de Koutcha, déjà plusieurs fois rencontré à toumchouq: le décor en lambrequin."
  9. Les résultats des analyses en microscopie électronique à balayage et les images obtenues en réflectographie infrarouge sont en accord avec l'emploi d'indigo. En réflectographie infrarouge, l'indigo est transparent. Afin de ne pas multiplier les prélèvements, la présence d'indigo n'a pas été confirmée par voie chromatographique.
  10. Sur la boîte aux oiseaux, l'analyse par fluorescence X met également en évidence du brome sur l'ensemble de la boîte. Est-il présent dans le colorant de la laque, dans le vernis? S'agit-il d'un matériau de restauration? Les analyses actuelles ne permettent pas de déterminer l'origine de cet élément.
  11. cf. note 1, T. Akiyama, op. cit. p 2. Les analyses ne mettent pas en évidence d'huile mais l'emploi de résine naturelle, gomme laque probablement.
  12. G. Béguin et J.P. Rioux, "A propos de deux couvertures de livre du XII<sup>ème</sup> siècle". *Revue du Louvre et des musées de France* (Paris, 1983), 5-12.



## Abstract

A variety of solid-state detectors (silicon, germanium, platinum silicide) were used to investigate the wavelength dependence of the visibility of a series of underdrawing materials over the spectral range 0.5–5.0 microns ( $\mu\text{m}$ ) in order to establish the optimal spectral band for infrared reflectography. Five reflectographs covering the spectral ranges of 0.5–0.8  $\mu\text{m}$ , 0.9–1.8  $\mu\text{m}$ , 1.5–2.0  $\mu\text{m}$ , 2.0–2.5  $\mu\text{m}$ , and 2.2–5.0  $\mu\text{m}$  were made of a test panel. The test panel consisted of a swatch of paint having a thickness of  $30 \pm 10 \mu\text{m}$  covering 8 different types of underdrawing lines. The results indicated that the wavelength of optimal visibility depends on the particular underdrawing material. For most underdrawing materials, optimal visibility is found at approximately 1.8  $\mu\text{m}$ . A slow fall off of roughly two-fold was seen from 2–5  $\mu\text{m}$  as the pigment appears to increase in opacity.

## Keywords

Infrared reflectography, imaging techniques, underdrawing, paintings, infrared detectors

## Examination of the Visibility of Underdrawing Lines as a Function of Wavelength

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## Introduction

Optimal performance of instrumentation for infrared reflectography (IRR) depends on two factors: spectral sensitivity and resolution. The pioneering studies by van Asperen de Boer identified the 1 to 3  $\mu\text{m}$  spectral region as optimal for the penetration of paints (1). The first step towards optimizing the system performance of an IRR camera is to identify detectors with high sensitivity in the spectral bands where the visibility of the underdrawing lines is best. The second is to maximize the contrast of small, closely spaced objects, such as hatch marks or fine lines. The spectral sensitivity of the detector is an intrinsic property. The resolution and contrast, however, depend upon the configuration of individual detectors. This configuration can either take the form of an array of individual detectors or a single element in which the image is scanned over the detector. For example, crosstalk between the detectors in an array can limit the contrast at the highest resolution. Recently, a detailed study of the resolution and sensitivity of two different types of detectors, a vidicon tube and a silicon Charge Couple Device (CCD), showed that the silicon detector possesses superior sensitivity and contrast (2). In that study, a vidicon camera was compared to a silicon CCD camera in detecting underdrawing lines over the same 0.7–1.1  $\mu\text{m}$  spectral band. The superiority of the CCD camera was attributed to its high light sensitivity, low noise, and high contrast at any resolution. However, the limited spectral sensitivity range of the silicon CCD camera precludes its use in IRR.

Spectral sensitivity curves generated in the study of the vidicon camera system (including the detector, lens, and lamp) showed that even though the detector is sensitive to 1.8  $\mu\text{m}$ , the dominant sensitivity of this system is in the range 0.7–1.2  $\mu\text{m}$ . This is because the signal from a fixed amount of light decreases approximately 50 fold from 1.0–1.8  $\mu\text{m}$  (2). Thus, a solid-state CCD camera having high spectral sensitivity in the 1.0–3.0  $\mu\text{m}$  range should perform better than the vidicon camera typically used for IR reflectography.

Recently, a variety of infrared-sensitive solid-state detectors have become available (3). We designed a series of experiments to identify the optimal spectral band for IR reflectography and to identify detectors suitable for constructing a new IR reflectography instrument that is optimized for the study of underdrawings on paintings.

Three different types of detectors were used in these studies. Two of the detectors were CCD devices: one made from silicon, which is sensitive from 0.4 to 1.1  $\mu\text{m}$ , and the other from germanium, which is sensitive from 0.7 to 1.8  $\mu\text{m}$ . Both of these detectors are very light sensitive: about ten-fold more than the vidicon at 0.9  $\mu\text{m}$ . The third detector, made from platinum silicide (Pt:Si), is a

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Schottky-Barrier detector and has the widest spectral sensitivity of the three (1.0 to 5.0  $\mu\text{m}$ ). However, the absolute light sensitivity of this detector is similar to that of the vidicon.

The studies were made using two commercial Pt:Si cameras to cover the 1.5 to 5.0  $\mu\text{m}$  spectral range and a homemade germanium scanner to cover the 0.9 to 1.8  $\mu\text{m}$  spectral range. A panel containing eight different underdrawing lines covered by a swatch of indigo paint was used as the test sample.

### Methods and Instrumentation

The CCD system consisted of a Sony XL 77 monochrome video camera. The vidicon system consisted of a Hamamatsu C1000-03 camera fitted with an N2606-10 lead sulfide tube, a Nikon 55mm macro lens, and a C1000-03 camera controller. The germanium IR scanner consists of a terrestrial telescope (10 cm focal length), a single germanium solid-state detector (SO#16471 EG&G Judson), and a homemade instrumental amplifier. An area of 1 mm<sup>2</sup> of the test panel is imaged onto the detector and the resulting photovoltage signal is read on a standard voltmeter. The Pt:Si system for the 1.5 to 2.5  $\mu\text{m}$  spectral band consisted of a Kodak KIR-0330 thermal imaging camera having a 640  $\times$  486 focal plane array. The camera was operated at 77°K with a variety of filters to define the spectral bands of interest. A Mitsubishi IR-M500 512  $\times$  512 Pt:Si camera was used to obtain the reflectographs in the 2.2 to 5.0  $\mu\text{m}$  spectral band. The images from the vidicon, silicon, and Pt:Si cameras were acquired either using a Macintosh IIfx (Apple) or a Quadra 700 (Apple), equipped with Scion and Perceptics Pixelbuffer framegrabber cards, respectively. A mock-up of a germanium image was constructed using the data from the scan to draw (in Photoshop) a small representation.

The test panel consisted of a hand-ground swatch of indigo oil paint (Kremer Pigmente) applied over 8 underdrawing lines on a gesso-coated 2  $\times$  2" microscope slide. The uniformity of the paint layer thickness was controlled by using a silk screen technique to lay down the paint.

The measured photosignals were normalized using the defined black and white regions of the test panels to facilitate comparison among measurements. The visibilities ( $\nu$ ) for each of the given underdrawing lines were calculated using the procedure described in Walmsley et al. (2). In brief,  $\nu$  is given by the equation  $\nu = (I_{\text{und}} - I_{\text{pig}}) / (I_{\text{und}} + I_{\text{pig}})$ , where  $I_{\text{und}}$  is the underdrawing peak height and  $I_{\text{pig}}$  is the pigment background height relative to the gesso. The visibility thus expresses not only the increase in transparency of the pigment but also any loss of absorbance by the underdrawing line.

### Results

All of the studies were performed on the test panel shown in Figure 1. The test panel has eight underdrawing lines of a variety of materials including red conte crayon, vine charcoal, mined black chalk, lead point, silver point, carbon black ink, and iron gall ink. The indigo paint layer was measured to be  $30 \pm 10 \mu\text{m}$  thick using standard cross section techniques. The images of the test panel were taken under conditions where the visibility of a given underdrawing line was not limited by the resolution of each camera.

The wavelength dependence of the visibility of the underdrawing lines was obtained using the silicon camera to cover the 0.5 to 0.8  $\mu\text{m}$  range, the germanium scanner to cover the 0.9 to 1.8  $\mu\text{m}$  range, and the Pt:Si cameras to cover the 1.5 to 5.0  $\mu\text{m}$  range. As expected, underdrawing lines were not seen from 0.5 to 0.8  $\mu\text{m}$  (Figure 1). However, the underdrawing lines are readily discernable in all of the reflectographs taken between 1.0 and 5.0  $\mu\text{m}$ , as is shown in Figure 2.

The reflectographs show an increase in the contrast of the underdrawing lines in the 1.5 to 2.0  $\mu\text{m}$  spectral band, as compared to the 0.9 to 1.8  $\mu\text{m}$  and 2.0 to 5.0  $\mu\text{m}$  bands. The graphs associated with each picture show this dependence more clearly and allow a quantitative comparison.

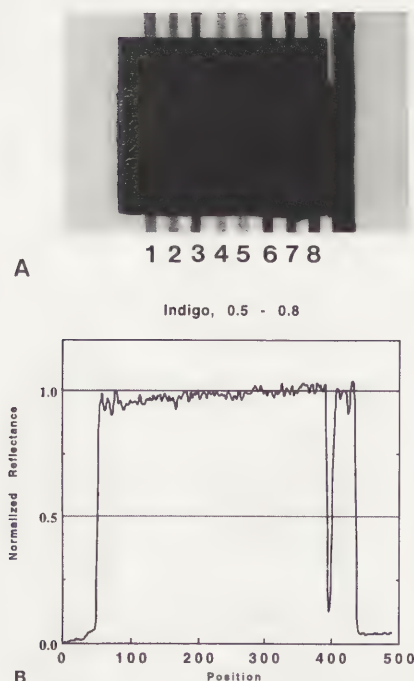


Figure 1. Picture of the indigo test panel taken in the visible portion of the spectrum (0.5 to 0.8  $\mu\text{m}$ ) with the silicon CCD camera. The numerical labels correspond with tested materials as follows: (1) red conte crayon; (2) vine charcoal; (3) black mined chalk; (4) silver point; (5) lead point; (6) carbon black ink; (7) mixture 1:1 of iron gall and carbon black ink; (8) iron gall ink. A graph of normalized reflectance is presented in panel B.



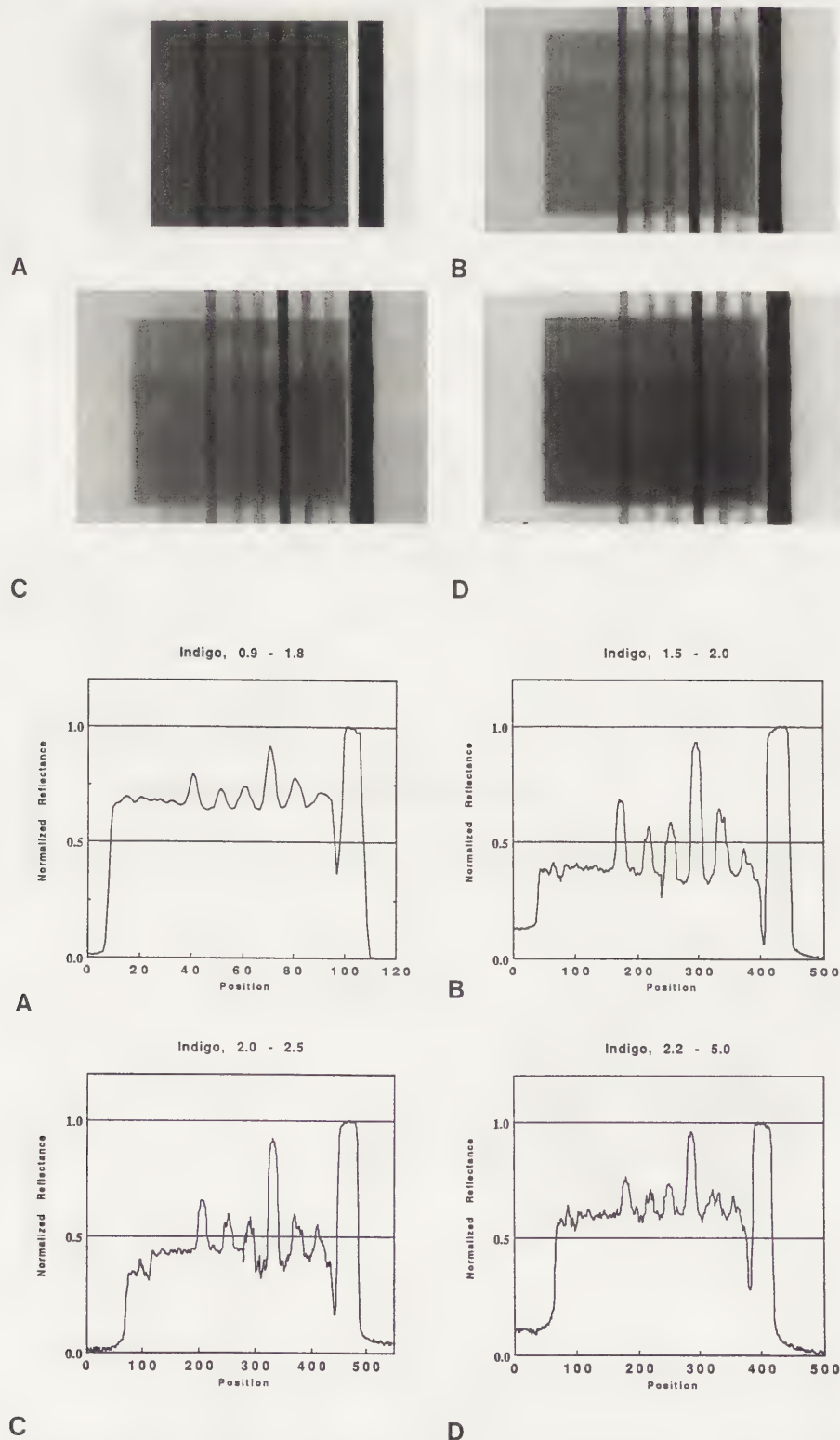


Figure 2. Images and mock-up (Top panel) and graphs (Bottom Panel) of the indigo test panel taken over four different spectral bands with the germanium scanner and the Pt:Si camera. A) Germanium scanner with 87a Filter (0.9 to 1.8  $\mu\text{m}$ ); B) Pt:Si camera (1.5 to 2.0  $\mu\text{m}$ ); C) Pt:Si camera (2.0 to 2.5  $\mu\text{m}$ ); D) Pt:Si camera (2.2 to 5.0  $\mu\text{m}$ ). The germanium data was used to construct a small mock-up of the test panel in Adobe Photoshop.

The graphs represent the intensity values of the individual "pixels" oriented horizontally across the reflectographs. Comparing the graphs of the 0.9 to 1.8  $\mu\text{m}$  data to that of the 1.5 to 2.0  $\mu\text{m}$  data, an increase in the height of the underdrawing lines, over the paint layer, is seen. The graphs from 2.0 to 5.0  $\mu\text{m}$  show not only that the height of the underdrawing lines decreases, but that the height of the paint layer also appears to increase. Upon closer inspection,

the amount of decrease in height of each of the underdrawing lines is different. Examination of the visibility,  $v$ , (see Methods and Instrumentation for definition) of each line for each spectral band shows this effect more clearly. A summary of the visibility for 6 lines for each spectral band is given in Table I. For example, iron gall ink decreases 3-fold while carbon black ink decreases only 1.7-fold. Thus, visibility of underdrawing lines depends not only on the transmittance of the paint layer, but also on the absorbance of the underdrawing line itself.

Table I. Calculation of underdrawing visibility.

Underdrawing	Wavelength (microns)								
	1.0	1.5	2.0	2.5	3.0	3.5	4.0	4.5	5.0
Mined Black Chalk		0.18		0.42		0.38		0.23	
Lead Point		0.13		0.28		0.30		0.16	
Silver Point		0.15		0.30		0.26		0.20	
Carbon Black Ink		0.30		0.60		0.54		0.39	
Carbon Black & Iron Gall Ink		0.18		0.40		0.30		0.14	
Iron Gall Ink		0.09		0.25		0.25		0.12	

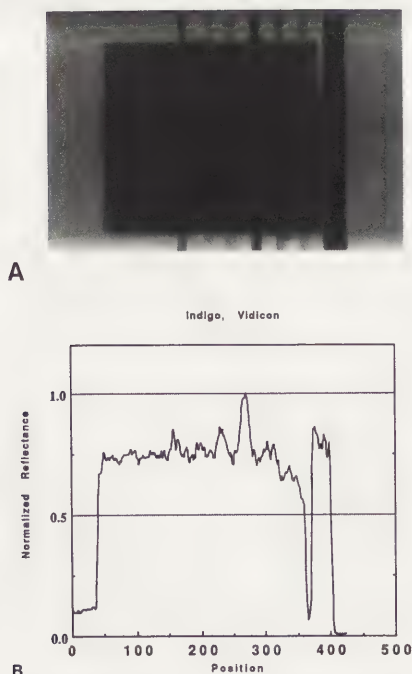


Figure 3. Reflectograph (panel A) and associated graph (Panel B) of test panel taken with IRR vidicon camera using the 87a Wratten filter.

It should be noted that images were collected in the 1.5 to 2.0  $\mu\text{m}$  spectral band for both the germanium and Pt:Si system to ensure that the observed effects were not detector-dependent. Identical visibilities for underdrawing lines (3–6, <3% variation) were obtained with the two detectors, indicating no detector effect was observed.

To place these results in a context directly understandable to a conservator or art historian familiar with images obtained with vidicon cameras, a picture of the test panel was made using such a camera with an 87a Wratten filter (Figure 3). As seen in both the reflectograph and associated graph, there is a significant decrease in the visibility of the underdrawing lines as compared with the Pt:Si cameras. In fact, the visibility of the most prominent line in the vidicon image is less than one half that observed with the Pt:Si or germanium detectors.

### Conclusions

The study of the wavelength dependance of the visibility of underdrawing lines over the spectral band of 0.9 to 5.0  $\mu\text{m}$  shows that for the majority of underdrawing materials, optimum visibility is achieved around 1.8  $\mu\text{m}$ . However, it is clear that particular materials have quite distinct behavior in the infrared spectrum, and optimal spectral bands will have to be determined empirically.



Comparison of different detectors shows that both germanium and Pt:Si are superior to vidicon tubes for the detection of underdrawing lines. As such, this paper details the instrumentation and methodology which underlie dramatic improvements in the usefulness, power, and reliability of the technique of infrared reflectography.

### Acknowledgements

We acknowledge partial funding for the project from the Circle of the National Gallery of Art. We also acknowledge Raymond Rehberg of Eastman Kodak (Electro-Optics Division) for the reconfiguration and loan of the Kodak PtSi Infrared Camera System loan, as well as Michael Mays of Mitsubishi Electronics America, Inc. (Thermal Imaging Products) for the loan of the Mitsubishi Thermal Imager IR-M500.

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## Abstract

The scientific investigation of a gold-printed and two silver-printed textiles dated to the 12–14th centuries yielded interesting results: copper has been used for gold, and tin for silver. The scanning electron microscopy and energy-dispersive spectroscopy x-ray analysis of other metal-printed textiles from the same period revealed that all but three were printed with brass or tin powder. In the case of the three exceptions, silver-gold alloys with relatively high gold content were identified. According to the results of the staining tests, proteinaceous and resinous materials were used for fixing the silver powder onto the surface of the textile yarn. Whether or not the examined textiles, or part of them, are forgeries, cannot yet be determined. Further investigations are needed.

## Keywords

Metal-printed textile, mediaeval, investigation, SEM-EDX method, forgery, brass powder, tin powder, silver-gold alloy

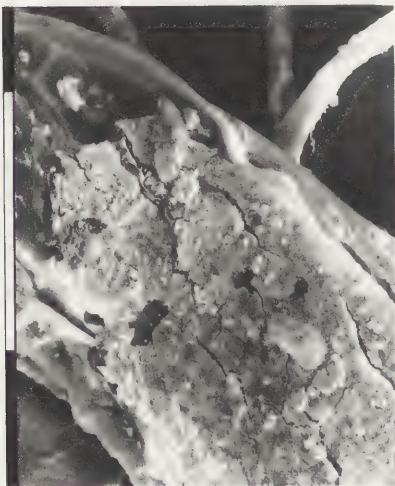


Figure 1. Metal-covered part of a silk yarn taken from a "gold-printed" textile (silver-gold alloy). Sample No. 1150. Scale bar: 0.1 mm.

## Genuine or False? Investigation of Metal-printed Textiles Dated to the 11–15th Centuries

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## Introduction

The first textiles decorated with block-printed gold or silver patterns appeared in Europe as early as the end of the first millennium A.D. (1). The technique of block-printing originates from Asia, and the first metal-printed textiles had probably been imported to Europe from the Near East (2,3).

A manuscript of the St. Catharina Monastery of Nuremberg was given to one of the nuns by the abbess in the 16th century. The manuscript describes the process of block-printing with gold and silver (Chapters XXXVI–XXXVIII):

The surface of the wooden printing block (the contours of the carved-in pattern) has to be spread with a sticky paste containing varnish (firnis), mastic, lead white, and yellow ochre (in the case of silver-printing, no yellow ochre is added). Turpentine and starch can be mixed to the paste, but it is not necessary. The printing block is then pressed onto the surface of the textile impregnated with glue. Before the paste has become dry, gold or silver is spread over the textile. After drying, excess metal can be brushed off (4).

According to Forrer, who first published the text, the manuscript can be dated to the 15th century; the recipes reflect the tradition of earlier times (5).

As far as we know, King was the first expert to doubt the authenticity of printed textiles of Middle European origin dated to the 11–14th centuries. These pieces appeared in great numbers on the art market in the second half of the 19th century. His investigations showed that most of them were forgeries (6).

After reviewing King's investigations, we examined six printed textiles dated to the 12–14th centuries in the collection of the Museum of Applied Arts, Budapest, Hungary. We found that copper was used instead of gold, and that tin replaced silver (7).

Since that time we have examined other metal-printed textiles dated to the same period (See fig. 1). The aim of our investigation was to answer the following questions. Are there any textiles printed with gold or silver powder among the sampled pieces (of European or unknown origin), dated to the 11–15th centuries? If so, was the process of printing similar to that described in the manuscript of St. Catharina monastery? Did the use of less noble metals instead of gold and silver occur among the samples examined? If so, are the analytical data sufficient for saying whether these textiles are forgeries?

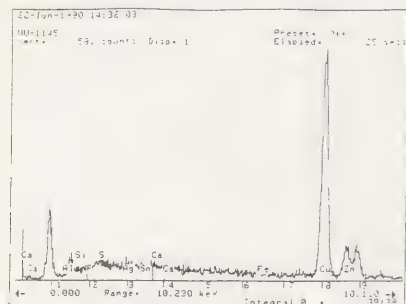
## Sampled textiles

Nineteen of the metal-printed textiles investigated recently are dated to the 11–15th centuries (according to the museum inventories). In most of the cases their origin is unknown. They belong to the textile collection of the Germanisches Nationalmuseum, Nuremberg, Germany.

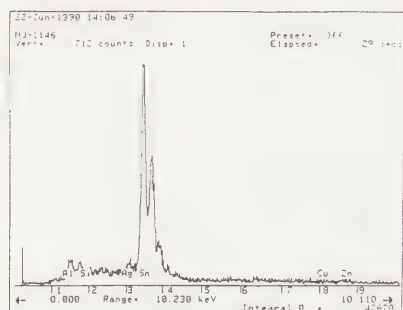
According to the descriptions, nine of them are gold-printed, one is printed in red on a gold background, one is painted or printed in gold, and eight are silver-

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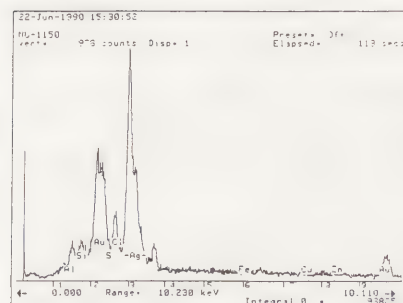




Sample No. 1145, EDX diagram



Sample No. 1146, EDX diagram



Sample No. 1150, EDX diagram

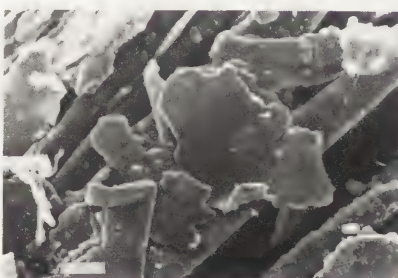


Figure 2. Metal flakes on the surface of the silk yarn (Sample No. 1108). Brass. Scale bar: 0.01mm.

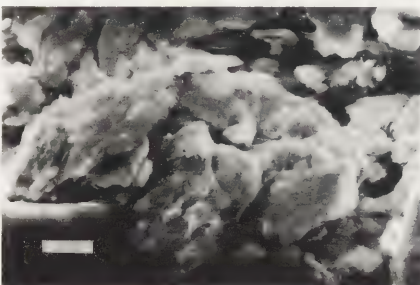


Figure 3. Corroded metal flakes on the surface of the linen yarn (Sample No. 1145). Brass. Scale bar: 0.01 mm.

Table I. Data on the examined textiles and results of the surface analysis.

Inv. no.	Description of the textile (according to the inventory data)	Date	Origin	Identified metallic elements
1100	Silver-printed red silk	11–12th c.	Cologne?	Sn
1101	Silver-printed brownish (originally red) silk	11–12th c.	lower Rhine area	Sn
1102	Silver-printed blue linen	12th c.	?	Sn
1107	Silver-printed blue linen	12–13th c.	?	Sn
1108	Gold-printed green silk	12th c.	?	Cu, Zn
1109	Green silk printed in black (originally silver?)	12–13th c.	?	Sn
1110	Gold-printed green silk	12–13th c.	?	Cu, Zn
1112	Gold-printed (or painted?) blue silk	12–13th c.	?	Cu, Zn
1113	Gold-printed brownish silk	12–13th c.	?	Cu, Zn
1115	Gold-printed green silk	12–13th c.	?	Cu, Zn
1118/ 1119	Pink silk covered with gold and printed in red	12–13th c.	?	Ag, Au
1124	Gold-printed reddish linen	13–14th c.	?	Cu, Zn
1145	Gold-printed blue linen	early 14th c.	lower German area	Cu, Zn (See fig. 2)
1146	Silver-printed blue linen	14th c.	?	Sn (See fig. 3)
1149	Gold-printed reddish linen	14th c.	?	Ag, Au
1150	Gold-printed green silk	14th c.	?	Ag, Au (See fig. 4)
1153	Gold-printed red linen	14–15th c.	Cologne	Cu, Zn

printed. Data on the textiles examined are summarized in Table I. The figures beside Table I show spectral data from energy-dispersive spectroscopy (EDX) surface analysis.

### Experiments

The joint use of a light microscope and an energy-dispersive spectrometer system attached to a scanning electron microscope (SEM-EDX method) provided the most useful information on the manufacturing technique of metal threads (8). The same methods have been employed for the morphological and material tests of the metal-printed thread samples.

A part of each sample (3–5 mm in length) was mounted onto a sticky surface for study and documentation under a light microscope (low magnification). The same mounted sample was used for surface analysis (morphology and identification of the metal) by SEM-EDX. Some of the samples were embedded in synthetic resin and polished to obtain a cross section. In the cross section we studied the structure of the printed layer, made the quantitative analysis of the metals, and tried to identify the type of binding medium by microscopy staining tests used in paint analysis (9).

### Morphology of the metallic surface

An examination of the surface at higher magnification (200–1000 times) shows that the quality of the metal powder and the quantity of the binding medium are different. In some cases, fine metal powder (small, thin metal flakes) is attached to the textile yarn with a small amount of binding medium (See fig. 2). In other cases, the metal-printed part looks like a broken piece of glue mixed with corrosion products (See fig. 1). In some cases the corroded metal flakes are distinguishable (See fig. 3).



### Results of material tests

The identification of the main elements present in the printed layer was carried out by examining the surface of the mounted samples. The main metallic elements identified are shown in Table I. Tabulated data show that all but three of the "gold-printed/painted" textiles are in fact printed with metal powder made of a copper-zinc alloy. The quantitative analysis of the uppermost surface layer of some samples showed that the zinc content varies between 10% and 28%. These data are not highly reliable data; in the near future we would like to check the metal compositions over the cross section of the metallic layers.

In three cases, we have found gold and silver in the surface layer, which was greyish (sample No. 1149) or completely black (sample Nos. 1118/19 and 1150). These samples were embedded in synthetic resin for further investigation. According to the results of quantitative analysis, the metallic layer has already been transformed more or less into corrosion products. Sulphur and chlorine could be identified along the cross sections. Silver-gold alloys were used in all of the cases, the silver to gold ratios (averages of several measurements along the cross sections) were 4.5:1 (sample No. 1118/19), 5.2:1 (sample No. 1149), and 2.9:1 (sample No. 1150) (See fig. 4). In the case of all of the three samples, the metallic layer directly covered the surface of the textile yarn.

A larger amount of proteinaceous material (binding medium) could be identified between the metallic surface and the yarn with samples No. 1118/19 and No. 1149. The protein test (staining with Amido Black 2 or with Fuchsin) was positive for the textile yarns as well, which has no meaning with sample No. 1118/19, because it is printed on silk. Sample No. 1149 gave a positive resin test as well (staining with a Bromocresol Purple solution). This test was negative with sample No. 1118/19. The oil test (staining with Sudan Black B) gave uncertain results; some coloration could be seen among the textile fibres in the case of sample No. 1149. As we have already mentioned, these tests give only preliminary orientation and cannot be used, for instance, when the original colour of the examined layer is similar to the colouration caused by the reagent (as it was the case with sample No. 1150, printed on dark green silk). We could not identify any inorganic elements that would indicate the addition of inorganic materials (pigments or drying additives) to the binding medium.

### Conclusions

The results of the analyses show that three of the examined textiles were printed with silver powder containing a higher amount of gold. We do not know the reason for the use of this alloy instead of pure silver; probably it gave a different colouration (but not that of gold). It is interesting that von Wilckens mentions two green silk fragments from Fritzlar dated to the first half of the 15th century, saying that they are printed in black, probably originally in gold (10). Was the metal powder used for printing these textiles similar to those found in our samples? Why does she think that the gold-printing turned black? The answers to these questions could probably help us to learn more about the use of silver-gold alloys for printing.

The process of textile printing of the textiles for our three silver (with gold)-printed samples was different from that described in the manuscript of St. Catharina Monastery. The binding media used for fixing the metal powder to the surface of the textile could have been a mixture of proteinaceous and resinous materials (sample No. 1149). Such mixtures were commonly used in the Middle Ages (11, 12). We can also suppose that the textile had been prepared with glue for printing, and that the binding medium was a resinous material or a mixture. An analysis of samples coming from the unprinted parts of the textile could clarify the problem. In the case of the other sample examined (No. 1118/19), only proteinaceous material was used as binding medium, according to the staining test results. Whether these textiles are genuine or not, we cannot answer yet.

In the future, we would like to analyse printed textiles considered by art historians as genuine to determine whether they were really printed with gold or silver and whether silver-gold alloys were commonly used for printing.

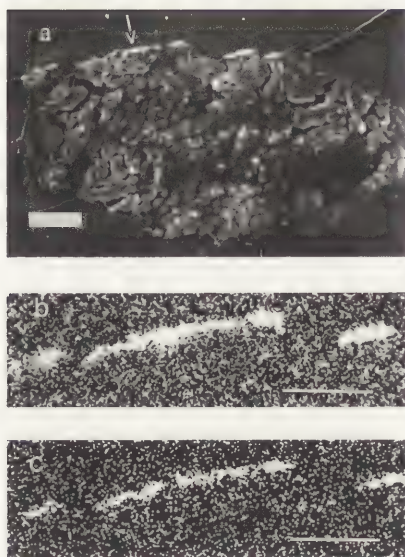


Figure 4. (a) SEM photograph of the cross section of Sample No. 1150, (b) Silver-specific picture of the upper part of the thread, and (c) Gold-specific picture of the upper part of the thread (scale bar for a, b, c: 0.1 mm).



Eight of the "gold-printed/painted" textiles examined proved to be "brass-printed." Copper alloyed with zinc has been used for gold imitations (e.g., in making coins or jewelry) for a long time (13, 14). We cannot exclude the possibility of the use of this relatively cheap material for replacing gold on pieces which, themselves, were imitations of expensive textiles woven or embroidered with gold threads. Theophilus Presbyter has already mentioned that silver, brass, and copper can be ground similarly to gold (15). But as far as we know, there is no hint in the special literature (neither in contemporary written sources, nor in the books or articles published in the 19–20th centuries) on the use of brass powder on paintings, in books or on textiles (16). This could be the result of a lack of research, but also supports the King's statement that these textiles are forgeries (17).

The eight "silver-printed" textiles are, in fact "tin-printed." The use of tin foil for replacing silver was suggested by Theophilus Presbyter as far back as in the 12th century, or by Cennini in the 15th century, among other centuries (18, 19). Theophilus mentions the grinding of tin as well (20). So the fact that we have found tin instead of silver does not prove that these textiles are forgeries. We have to carry out the same investigations, as in the case of the "brass-printed" ones.

In the future, we would like to analyse the pigments, if there are any, of the "brass-printed" and "tin-printed" textiles. If we can find 19th-century pigments together with brass or tin powder, we should get nearer to the solution of the problem: Are these textiles genuine or forgeries?

### Acknowledgements

The authors are grateful to textile restorers Ms. Annelise Streiter and Ms. Erika Weiland at Germanisches Nationalmuseum, Nuremberg, for the samples and for their help in the work. Thanks are due to Ms. Márta Kiss-Bendefy, a chemist at the Hungarian National Museum, Budapest, for the identification of the binding media, and to Ms. Erzsebet Gondár, a chemist at the Textile Research Institute, Budapest, for the SEM photo in figure 4.

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## Abstract

A new IR-vidicon TV camera QVC-2500 (QUANTEX Photonic Products) was equipped with a bandpass interference filter to eliminate chromatic aberration from standard photo lenses in the infrared (IR). It provides a horizontal resolution of 650–700 TV lines based on visual observation of a standard TV test chart. The improved resolution (2 to 3 times better in comparison with the commonly used Hamamatsu vidicons No. 2606-06 or older model No. 214-06) permits the operator to reduce the number of reflectographs by a factor of up to 5, thereby significantly simplifying the assembly procedure for the set of individual reflectographs. The ability to reveal covered details with the new camera is also much improved because it works in the longer IR wavelength region circa 1620 nm (or 1800 nm), in comparison with the standard Hamamatsu cameras which provide an effective spectral response centered at wavelengths less than 1300 nm due to the poor choice of a filter that cuts off wavelengths less than 1000 nm. The price of this equipment is 50–75% of that of the standard Hamamatsu set.

## Keywords

IR-reflectography, TV camera, vidicon, TELTRON TV2201, resolution, lenses, chromatic aberration, bandpass interference filters, ORIEL, infrared imaging

## An Improved Vidicon TV Camera for IR-Reflectography

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## Introduction

The IR (infrared) TV cameras, equipped with the Hamamatsu No. 214 or No. 2606 vidicons and " $\lambda \leq 1000$  nm" cut-off filters (Kodak No. 87C, Toshiba IR-D80A, RG-1000, etc.), are commonly used in art museums. As numerous estimates show, the average horizontal resolution reached by such systems is only 250–350 TV lines. This low resolution of existing IR-reflectography causes the need for assembling fragments usually not larger than  $10 \times 10$  cm. This disadvantage makes IR-reflectography a very time consuming and labor intensive task: analysis of just one painting measuring  $1.0 \times 1.0$  m requires that more than 100 reflectographs be taken and assembled. From this point of view, the improvement of the IR image definition becomes an important task in modern museum IR-reflectography. The considerable progress made in the development of this technique will be demonstrated.

The resolution of a TV closed circuit system is limited by the resolution of the optics, the resolution of the vidicon itself, the frequency band-pass of the video amplifier, and the resolution of the monitor.

In the visual range standard lenses normally deliver about 40–50 pairs (black and white) of lines per mm, which corresponds to a potential horizontal resolution of 1016–1270 TV lines on the target for 1" vidicon. Therefore the lenses are never considered to be the critical element in the chain and are commonly ignored by the TV electronics designers. In the infrared, however, the situation is different: this aspect will be discussed in some detail.

The band-pass of most video amplifiers installed in standard TV cameras is 10–12 MHz, sufficient to channel the TV signal (625 lines/50 Hz or 525 lines/60 Hz, 2:1 interface) with the resolution of 650–800 pixels along the TV raster line. The black and white monitor does not normally restrict the channel resolution either, since even the older models could easily produce 750–900 TV lines.

The really critical link in the closed circuit TV systems is the vidicon itself. After Hamamatsu Photonics Co. advertised the No. 214-06 tube in the 1970s (sensitive up to a wavelength of 2200 nm with a resolution of approximately 700 TV lines on the target), the logical expectation was that the same resolution could be reached in IR-reflectography (1). In fact nothing like that has become possible, for the several reasons which will be discussed below.

## IR-vidicon limit resolution

The amplitude response (AR) of the typical No. 2606-06 Hamamatsu vidicon is represented in Figure 1, graph 1, as given in the manufacturer's technical sheet (2). As can be seen at the limit level of about 4–5% modulation (determined by a signal-to-noise ratio of 20–25, inherent for most IR-vidicons), the resolution in TV lines should reach approximately 600. The author tested No. 2606-06 in 1987 on the special equipment in the Television Institute in St. Petersburg, Russia, and found that the resolution of the tube in reality was only 500–550 lines in the center of the target and 350–400 lines in the corners, i.e., 10–15% lower than advertised. (Even those figures could only be reached by using filtered light, in the visual range). The basic resolution provided by the same tube in the Hermitage Museum laboratory TV system in the infrared with 1700 nm cut-off interference filter and special quartz/fluorite lenses (Russian model ZI-KAR 1A, 1:1.1, 100 mm, corrected in the range 1100–2200 nm) and measured with a standard TV test chart was about 350–375 lines. This figure is much worse than that of a Russian-made vidicon LI434, which under the same conditions provided a resolution of 500–550 TV lines, a result that seemed at that

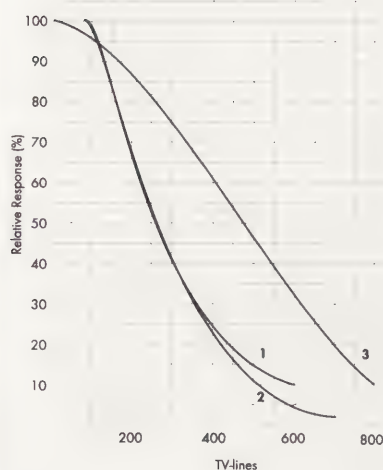


Figure 1. The amplitude resolution of the IR vidicons. 1) Hamamatsu No. 214-06, 2) Hamamatsu No. 2606-06; 3) Teltron TV2201.

time to be a record. When the No. 2606-06 was tested using the standard photographic lenses with apertures of 1:2–1:8 and a 1000 nm cut-off filter, the resolution dropped to 280–300 TV lines, which has been the standard figure in museum IR-reflectography.

Two major conclusions followed from those experiment. The Hamamatsu No. 2606-06 vidicon did not provide the advertised resolution under experimental IR-reflectography; the actual figure was determined to be only half of that promised for the vidicon. Secondly, the application in the IR of the standard photo lenses designed and corrected for aberrations in the visual region with 1000 nm cut-off filter leads to an additional 20% loss of resolution.

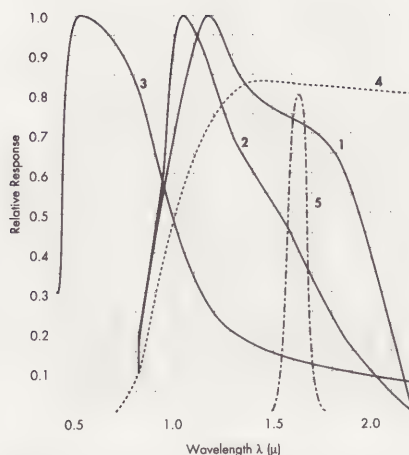


Figure 2. Spectral response of IR vidicons. 1) Hamamatsu No. 214-06, 2) Hamamatsu No. 2606-06, and 3) Teltron TV2201.

### A breakthrough

In 1992 the Quantex Corp. (Rockville MD, USA) advertised the IR TV camera QVC-2500 with a spectral response up to 2500 nm based on a 1" vidicon tube (model TV2201 Teltron, PA, USA). The specified resolution is considerably better than that of Hamamatsu No. 2606 (3). Figure 2 represents the corresponding data for the vidicons of both manufacturers. From the graphs one can conclude that the resolution of the Teltron vidicon at a level of 10% modulation is 800 TV-lines, while the Hamamatsu provides at the same level only 500 TV-lines. The spectral response of the Teltron at 2200 nm wavelength relative to the maximal response (at 500–600 nm) drops 13 times, while for the Hamamatsu the corresponding figure is 70(!), the maximal response of the latter tube being at 1000–1100 nm. The absolute figures for both tubes' sensitivities are difficult to compare; Hamamatsu Co. provides the vidicon signal current as a function of illuminance (lux) on the surface of a Toshiba IR-D80A filter, i.e., in nA/lux, while Quantex Corp. provides the dependence of the signal current on illuminance of the target measured in "IR lux" using the 2870°K tungsten source, i.e., after the irradiation has passed through the "No. 205" filter which is unknown to the author as a standard filter.

Furthermore, the spurious signal specifications, i.e., the number and size of defect spots on the target, is approximately at the same level for the Teltron as for the Hamamatsu No. 2606 series.

Considering the above information, the Teltron vidicon appeared to have advantages for use in IR-reflectography over the Hamamatsu. The only serious problem to be solved was the selection of an acceptable optical compromise (primarily to correct chromatic aberrations), since to the best of our knowledge no manufacturer in this country is marketing lenses corrected in the near IR 1000–2000 nm range.

### Optical resolution of photo lenses in the near IR

The Hamamatsu Application Note 4001 reads: "No attempt is made by optical designers to correct lenses for chromatic aberration in the infrared. . . . To expect any lens to focus the entire 1 to 2 micron band simultaneously is unrealistic. For temperature measurement, low-resolution wide bandwidth imaging may be suitable. For most other purposes (including IR-reflectography!- author's comment), the bandpass must be restricted to produce adequately sharp images" (4).

This passage formulated in 1981 contains sufficient explanation for many observed problems in museum IR-reflectography. The filter with a cut-off at about 1000 nm (Toshiba IR-D80A or similar) plus the use of standard photo lenses in the Hamamatsu cameras have caused major drawbacks. There is no mention in literature of anyone trying "to restrict the bandpass" or even to measure the actual resolution just to check the promised resolution of 450 TV lines. The practical consequence was a universal lack of definition in the IR images, which in turn led to complicated fragment-assembling procedures. More recently the assembly has been computerized or even automated, using Amparo or Vasari-type editing software packages. However, it seems that improvements in assembling dozens of reflectographs have obscured in some way a much more natural and promising computer application-image processing aimed at additional increase in the contrast of structures revealed under the paint layers.



One of the major optical drawbacks is that the lenses deliver the reflectographed object image with a resolution lower than the vidicon is capable of providing. Secondly, the effective wavelength used for reflectography with the 1000 nm cut-off filter installed in the camera is not optimal for revealing certain details, in particular charcoal/carbon underdrawings.

In order to demonstrate how a poor choice of optics affects the Hamamatsu No. 2606-06 vidicon some semi-quantitative estimates can be made.

First of all, it will be helpful to calculate the optical resolution for lenses corrected for the visual range when these lenses are used for imaging over a broad range of the vidicon spectral response, for instance in the range 1000–2000 nm. Estimating this resolution is a rather complicated task. To do so requires information on the optical scheme, the focal distances of the individual lens elements, and knowledge of the refraction index dispersion for the lens glass; the latter is not always available for the IR. For these reasons the problem must be confined to a semi-quantitative solution using certain assumptions. As the "objective lens" we assume the use of a typical achromatized doublet (crown glass/flint glass pair of positive and negative lenses) with a focal distance ( $f$ ) calculated at 589.3 nm, the doublet having been corrected in the visual range at the end points of an interval 486.1–653.3 nm (5). Following the procedure used by this author, it is possible to calculate the defocusing (the geometric size of the image of an infinitely small object/point source as formed in the focal plane by the doublet sharply focused, for example, at 1000 nm wavelength, i.e., at the maximum of the spectral response of the Hamamatsu vidicon) (6). The defocusing in the focal plane ( $\rho$ ) may be determined from the approximate expression:

$$\rho = \Omega (df) \quad (1)$$

where  $\Omega$  is the lens system aperture, ( $df$ ) the increase of the focal distance ( $f$ ) of the doublet due to the negative dispersions of refractive indices of the optical glass under the change of the wavelength from 1000 nm to 2000 nm.

If we accept the same dispersion values as in (6), the calculated change of the focal distance ( $f$ ) is:

$$df = 0.015f, \quad (2a)$$

and we have from (1):

$$\rho = 0.015\Omega f \quad (2b)$$

From (2b) it immediately follows that the optical resolution in the IR for photographic lenses with focal distance  $f = 50$  mm, even using a relatively small apertures of  $\Omega = 1/8$ , is only  $1/\rho = 11$  lines/mm in the focal plane, i.e., in our case on the vidicon target.

The normal target (sensor) size for 1" vidicon is  $12.7 \times 9.5$  mm, from which it follows that the limit of the optical horizontal resolution is only  $H = 12.7 \times 11 = 139.7$  lines, a value which would normally be associated with the limit of the TV resolution of about 200 TV lines on the standard TV test chart projected by the lenses on the vidicon target (7).

Smaller apertures, such as 1:22, can provide better optical resolution of up to 550 TV lines. The use of very small apertures, however, may increase the necessary illumination of the painting to unacceptably high levels. A noticeable decrease in the image brightness (vignetting) from the center to the edge (approximately as  $\cos^3(\Omega/2)$ ) takes place as well.

Expression (2b) also indicates that the optical resolution is inversely proportional to the focal distance of the lenses, and, consequently, the wider angle lenses should provide better results in the IR in comparison to the normal or, notably, the telephoto lenses.

### Spectral range

In addition to the poor resolution, there is another major drawback of the existing Hamamatsu IR-reflectography equipment: the use of a 1000 nm cut-off filter

installed "to block the visual range." The evident consequence of the use of this filter is the loss of the system's ability to penetrate in the IR, i.e., the decrease of the so-called "hiding thickness" of the paint layer covering the charcoal underdrawing to be revealed (8). To demonstrate such an effect we need to apply the theory of IR-reflectography discussed in the literature (9,10).

It was shown that in the regions of the infrared where bands of IR absorption by pigments or binding medium are absent. Consequently, where only the diffusion of the IR-irradiation affects the flux extinction, the transmission factor begins to increase extremely fast (as the forth power of the wavelength or even faster), as the wavelength of irradiation  $\lambda$  becomes greater than  $\lambda_0$ :

$$\lambda_0 = D(n-1), \quad (3)$$

where  $D$  is the dimension of the pigment grain measured in the direction of incident irradiation propagation, and  $n$  is the ratio of the refractive indices of the pigment and medium.

Provided that the statistical distribution of pigment grains (grain-mass distribution) is Gaussian, the theoretical analysis predicts that the *transmission factor of the paint layer grows linearly with the wavelength*. This conclusion has been confirmed experimentally (9).

Depending upon the scattering properties and thickness of the paint layer, the ground of the painting and the underdrawing, three different situations were predicted: 1) the contrast of the underdrawing (covered with a paint layer) may increase continuously with the increase of the wavelength; 2) the contrast of the underdrawing may reach a maximum at a certain optimal wavelength ( $\lambda^{\max}$ ); and 3) the underdrawing may not be revealed at all in the IR at the given level of detection ability (signal/noise ratio) for the reflectography system.

It was shown that the carbon-containing underdrawing on a thick chalk or gypsum painting ground corresponds to the situation 1, since the carbon absorption factor is close to 1 in the whole range of the near IR. Consequently, in the range of spectral response of the vidicon, the longer is the wavelength, the better (10). Our preliminary experiments with the Mitsubishi IR-512-OC Thermal Imager indicated, by the way, that this conclusion may be extrapolated to the middle IR-region  $\lambda \geq 3000$  nm, this latter region providing even better revealing abilities than the near IR.

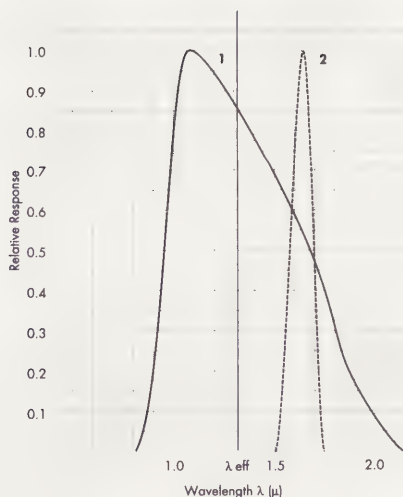


Figure 3. The influence of IR filter choice on the spectral response of IR vidicons. 1) Hamamatsu No. 2606-06 + Toshiba IR-D80A filter, 2) Teltron TV2201 + Oriel interference filter No. 56048.

From the graph of vidicon spectral response multiplied by transmittance of the Toshiba IR-D80A filter (See fig. 3, graph 1) it can be easily seen that the *effective wavelength* currently used for reflectography is only about 1320 nm, i.e., the widely advertized Hamamatsu vidicon spectral response "up to 2200 nm" is quite artificially and effectively suppressed by the filter choice. Furthermore, the use of conventional tungsten bulbs with temperatures of about 2800–2900°K for illumination, with spectral maximum of emission at 1000 nm, will additionally shift the effective wavelength even further into the shorter wavelength region. This type of "reflectography" delivers less revealing ability to the vidicon than conventional IR-photography would have if 1000–1100 nm sensitized commercially available films and the same Toshiba filter were used. This effect can be explained by the much higher detection limit of the films providing an equivalent signal/noise ratio of 45–50, while the IR-vidicons have this ratio of 30 or less (11). It was shown that the IR-vidicon can only reach the revealing ability of IR film I-1070 (Russian-made, sensitized with a maximum at 1070 nm) only at  $\lambda = 1400$  nm(!). The advantages of conventional IR photography would even be more pronounced when larger film formats were to be used to eliminate the fragment-assembling procedure altogether.

In summary, the application of the Hamamatsu IR-vidicon, in museums, "as is," appears to be restricted as a result of certain misunderstanding of the theory of IR reflectography both by the manufacturer's part and by the part of conservators and museum scientists. This misunderstanding has led to the underestimation of the potential of this very powerful and significant tool for the examination of works of art.



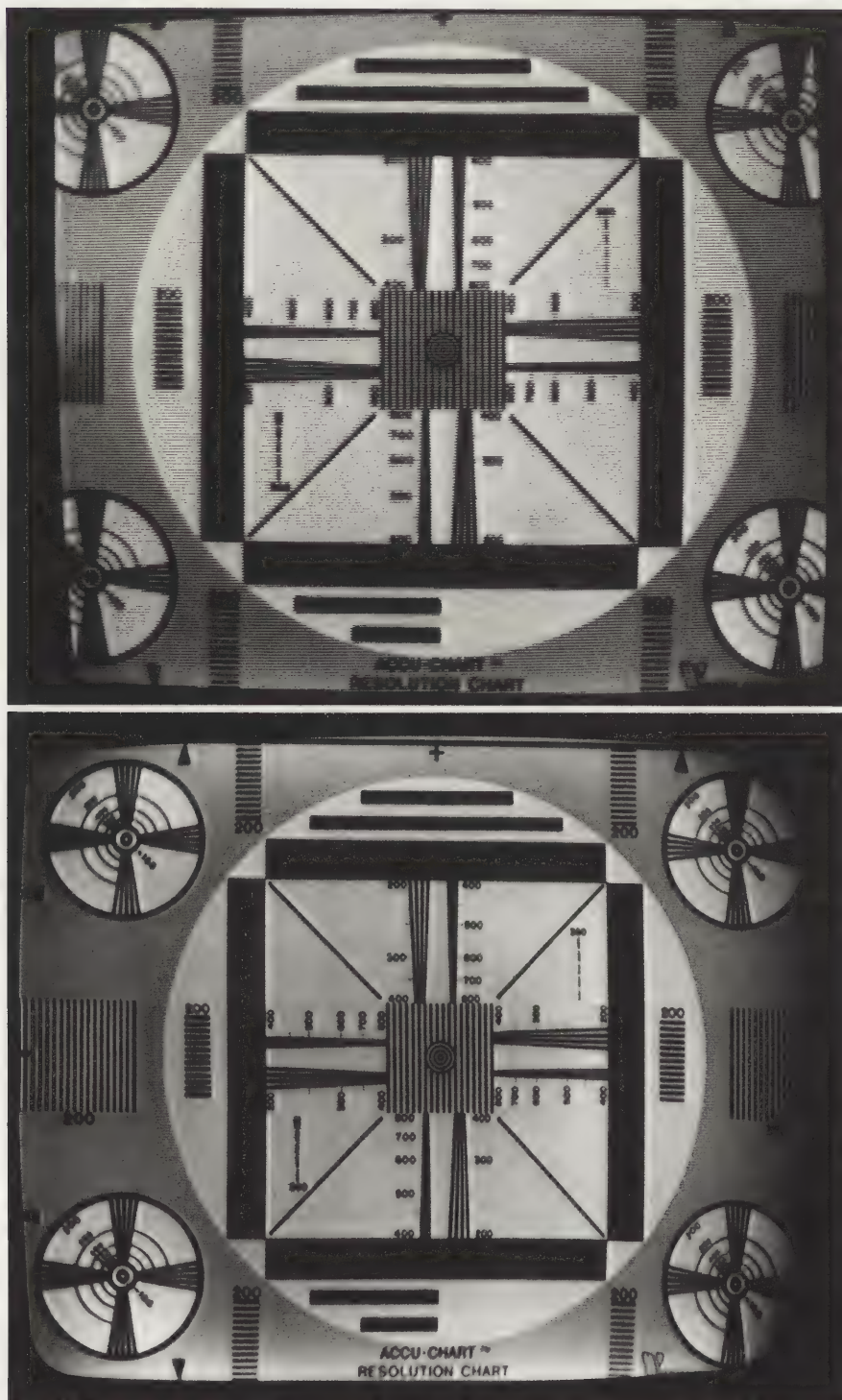


Figure 4. The standard resolution TV test chart as photographed on the monitor screen (note the resolution in the central wedges vertically and horizontally). 4a) Hamamatsu camera C1000-03, No. 214 vidicon + Toshiba IR-D80A filter (Courtesy of the Painting Conservation Department of the J. Paul Getty Museum), 4b) Quantex QVC-2500, Oriel No. 56048 filter.

### Optical solution

As indicated above, two main problems need to be solved: 1) the chromatic aberration of standard photo lenses in the IR must be minimized; and 2) the wavelength must be increased further in the IR-region to improve the revealing ability of the camera. Both problems can be solved simultaneously by application of a special interference filter with a *relatively narrow bandpass* in the IR-region. Among the filters suitable for the purpose are those available from ORIEL Corp., CT, USA, Cat. Nos. 58045, 58046, 58047, 58040, 58050, and 58060. These filters have a maximum transmission (50–80%) at 1500, 1600, 1700, 1800,



1900, and 2000 nm respectively and a band-pass half-width around 100 nm; the filters block short wavelengths (up to X-rays) and long wavelengths (up to 3500 nm).

The resulting relative spectral response of the Quantex/Teltron vidicon with the Oriel No. 58046 filter is shown in Figure 3, graph 2. The maximal response is at  $\lambda = 1630$  nm, the band-pass half-width being 102.5 nm as can be deduced from the precise spectral transmission curve supplied with the filter by the manufacturer.

The lens used on the Quantex QVC-2500 camera was a standard Nikon 50 mm, 1:1.8. An illumination level of 200–300 lux from standard tungsten bulb(s) on the surface of the object at the full aperture of the lens was sufficient to provide the normal amplitude of the video signal using the No. 58046 filter. When using the No. 58040 filter with a maximal transmission at  $\lambda = 1800$  nm, the illumination should be increased up to 500–600 lux.

The monitor used was a Panasonic model VW-5470, which permits the horizontal resolution of 850 TV lines and synchronizes with the US standard video signal (NTSC) of the camera-525 lines, 60 frames/s, 2:1 interlace (12).

The visual horizontal resolution of the system estimated with the chart test as it appears on the monitor screen is 650–700 TV lines (Fig. 4b), which is approximately 2–2.5 times greater than the corresponding resolution of the Hamamatsu vidicon system (compare with Figure 4a). Figure 5 provides a comparison of the revealing ability of both instruments with a test panel.

The fact that the obtained resolution hardly depends on the lens aperture confirms the satisfactory achromatization by the proper filter selection.

The maximum number of reflectographs that the new system permits the operator to take is only twenty percent of the usual number from one painting for assembly. If we accept that for a normal rendering of an underdrawing a resolution of 2–2.5 TV lines per 1 mm on the painting surface is sufficient, then the size of the fragment taken per reflectograph will be around  $30 \times 24$  cm. For example, it was possible to assemble the IR-image of a  $86.4 \times 55.6$  cm painting (attributed to H. Bosch, private collection), with 8 reflectographs, providing a clear and detailed image of the revealed underdrawing; another painting by Pieter Coecke van Aelst, *Adoration of the Magi*,  $90.6 \times 57.2$  cm, (Los Angeles County Museum of Art), needed only five reflectographs.

### Conclusion

The application of high resolution IR-reflectography provides numerous advantages as compared to the conventional Hamamatsu IR vidicons currently used by most investigators. There is less need for the computer to assemble the numerous reflectographs, leaving to the computer the more significant task of image processing aimed at increasing the contrast of the revealed underdrawing (frequency filtration using Fourier transforms, histogram procedures, etc.).

Further increases in resolution will be possible with the Teltron vidicon, primarily in the vertical direction using the TV standards with 625 (or more) lines per raster. The infrared wavelength may be further increased by choosing the appropriate interference filter from the ORIEL products mentioned above or similar band-pass filters from another manufacturer.

### Acknowledgements

I would like to acknowledge Dr. Pieter Meyers, the Head Conservation Center of the Los Angeles County Museum of Art, who demonstrated full understanding and cooperation and without whose help this work simply would not have been possible.

Comparison with the Hamamatsu system was made possible thanks to Mr. Andrea Rothe, Head of Painting Conservation at the J. Paul Getty Museum.

I would like to express my gratitude to John W. Twilley and Peter I. Dammers of the scientific staff of the LACMA Conservation Center for fruitful discussions on this subject.

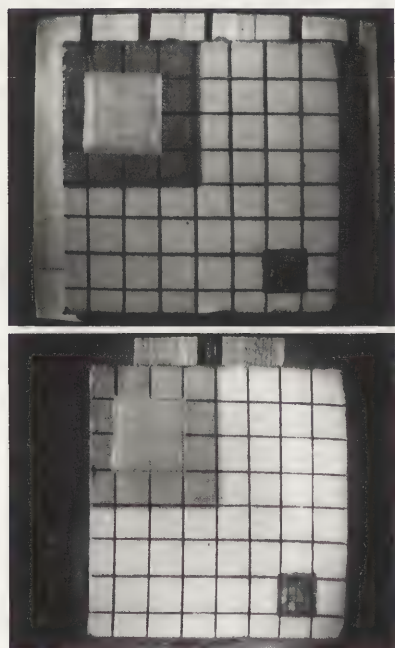


Figure 5. Comparison of the revealing ability of IR vidicon cameras regarding charcoal underdrawing over a thick (0.3 mm) gypsum ground; the underdrawing (grid) is covered with a layer of the mineral azurite (30 microns) on the lower right square and with two layers: 20 microns of azurite in oil and 80 microns of titanium dioxide in acrylic medium on the upper left big square. 5a) Hamamatsu C1000-03, No. 214 vidicon, Toshiba IR-D80A filter, 5b) Quantex QVC-2500, Oriel No. 56048 filter.



I appreciate the assistance of Ms. Shelly Svoboda who prepared the model painting sample, and the help of Ms. Emily Dunn in editing of this text.

### Notes

1. J.R.J. Van Asperen De Boer, "A Note on the Use of an Improved Infrared Vidicon for Reflectography of Paintings," *Studies in Conservation* 19, (1974): 97-99.
2. Hamamatsu Technical Data Sheet Super Infrared Vidicons N2606 Series, Hamamatsu Photonics K.K., Electron Tube Division, Feb. 1986. Hamamatsu Corp., 360 Foothill Rd., P.O. Box 6910, Bridgewater, NJ 08807-0910, USA.
3. QVC-1800 and QVC-2500 IR Sensitive Video Camera Systems Quantex Photonic Products, Quantex Corp., 2 Research Court, Rockville, MD 20850, USA.
4. Hamamatsu Application Note/4001, C1000-03 Infrared TV Camera p.7, Hamamatsu Systems Inc., 40 Bear Hill Rd., Waltham, MA 02254, USA.
5. Attention is given only to the chromatic aberration because all other types of aberrations (astigmatism, coma, distortion, spheric) belong to the 3rd order of smallness, while chromatic aberration due to the very wide region of vidicon spectral response is of the 1st order, affecting the image in the same way as the failure to focus the lenses properly.
6. A.J. Kossolapov, "Fizicheskie Metody Izucheniya Proizvedeniy Iskusstva" (Methods of Physics in Examination of Works of Art, in Russian) (Moscow: Iskusstvo, 1985), 59-66.
7. For a standard TV resolution chart (we used ACCUCHART from VERTEX VIDEO SYSTEMS (C) 1986, available in the USA from Nalpak Sales, El Cajon, CA 92020, USA) the resolution of 200 TL corresponds to 133 vertical black lines resolved on the chart in the horizontal direction (or 100 black horizontal lines resolved in vertical direction).
8. J.R.J. Van Asperen De Boer, "Infrared Reflectography" (Ph.D. diss., Groningen University, Amsterdam, 1970), 21, 35.
9. Kossolapov, "Fizicheskie Metody," 29-57.
10. This conclusion contradicts the results of Van Asperen De Boer (8), who believed that there is an optimal wavelength for the revealing of underdrawing at 1800 nm. This question will not be discussed here, for, even if one accepts De Boer's figure, it is still very far from the wavelength of 1320 nm selected due to the usage of a combination of the Hamamatsu vidicon and the  $\lambda \leq 1000$  nm cut-off filter.
11. A.J. Kossolapov, "Infrared Reflectography of Paintings: Theoretical and Experimental Research" (Paper delivered at the Sixth Triennial Meeting of the International Council of Museums Committee for Conservation, Ottawa, 1981), 1/1/3.
12. The camera QVC-2500 can also provide 625 lines 50 frames/s 2:1 interlace standard signal (CCIR), but this particular monitor WV-5470 may not be synchronized with the CCIR.

## Abstract

Ten samples of metal threads from 17th-century tents are examined and analyzed by optical scanning electron microscopy and ED X-ray fluorescence to determine the composition and method of wire manufacturing. Samples M1, M2, M4, and M9 contained silver and gold while samples M3 and M5 were found to contain only silver. It appeared that pure silver bar with about 1% copper was prepared and then gold leaf was wrapped prior to fusion and fine wires were drawn after heating. Metal threads or Jari were flattened either with power driven machine or by highly skilled craftsmen. All samples except M5 are cast, drawn, and hammered which also confirms manufacturing technique described in the literature.

## Keywords

Jari, wire manufacturing, Mughal tents, brocade textiles, silver-gold ratio, cross section, gold-silver boundary

## Scientific Examination of 17th-Century Metal Threads of Mughal Tents by Scanning Electron Microscopy and Energy Dispersive Spectrometry

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## Introduction

Gold and silver wires are the commonly used materials of both ancient and modern industries in India and are used in a wide variety of applications both decorative and functional. India was known for making gold and silver wires, called Jari, of such a fineness that entire fabrics could be woven from them. Jari industry reached its zenith during Mughal period and continued to flourish during British period. Jari is extensively used in embroidery works and weaving gold and silver brocades which are known to be used since 1st to 4th century (1). Ajanta wall paintings depict the use of brocade textiles (2). Megasthenes, an ambassador in the court of Chandragupta, during 302–208 BC has mentioned in his detailed account of India that in those days the Indians wore flowered muslins of the finest weave and ruling classes were clad in robes embroidered in pure gold (3). Various, old Indian literature mentioned the method of manufacturing gold and silver wire but detailed descriptions are found in the book of Gorge Watt (4) and recent monograph of census of India written in 1961 (5).

A brief on the technique of wire making as described in the census monograph is as follows. Silver was first converted into a rectangular bar (45 × 2 cm.) and gold leaf was wrapped. It was heated in a furnace at 960°C till the gold leaf was completely fused with silver bar. The bar having uniform coating of gold was hand drawn into wire by pulling it through a series of steel dies till wire as fine as human hair was drawn. It is interesting to note that a gold coating given to original silver bar used to remain uniformly on the wire. The resultant fine wire was then flattened by hammering on anvil. The flattening of the fine wire which was formerly done by manual labor is presently done with the help of flattening machine. In the hand operated units wire was further drawn by hand with the aid of dies on revolving wooden drums till the required fineness was obtained.

Although some works on the elemental analysis of metal threads in Indian brocade have been reported by Bhatnagar and Indictor et al. (6, 7), there has been a paucity of data on the technique of wire making in Indian medieval textiles. However, Darrah has studied the technique of wire manufacturing in 19th-century Indian decorative hats and Járó has extensively studied the wire making technology in European textiles (8–10). Therefore, the aim of the present study was to determine the compositional and technological aspects of metal threads used in 17th-century Mughal tents.

## Materials and methods

Samples were taken from two different Mughal Tents of the 17th century which belonged to Mehrangarh Fort Museum, Jodhpur, Rajasthan (India). The dimension of one of the tents was 720 × 720 × 600 cm (L × W × H) and it had two compartments. The inner side of the tent was heavily embroidered with floral designs. Sample nos. 1, 2, 3, and 4 were obtained from this tent. The other tent, known as 'Two poled embroidered Tent,' was quilted and embroidered in beautiful floral design. The sample nos. 5 and 9 were chosen from this tent.

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In embroidery work metallic threads are used besides cotton and silk but only metallic threads are selected for the present work. In this study, the samples were designated as M1, M2, M2A, M3, M3A, M4, M4A, M4B, M5, and M9.

The samples were first observed through a light microscope and then specially mounted on stubs with double sided scotch tape and coated with pure carbon fiber in a sputter coater (Biorad, ES-500). To obtain a cross section, flattened metal wrapping was mounted in embedding resin and ground on abrasive papers and finally polished. Samples were examined using scanning electron microscope (Philips, 515) and analyzed with energy dispersive X-ray system (PV-9900) which was attached with SEM. Operating conditions were given on the micrographs.

In each case, wrapping was separated from core fibre in a way which would allow viewing of (a) exterior metal surface, (b) interior of metal wrap, (c) core fibre and (d) cross section of core fibre. Using above methods it was possible to identify core fibre, main components of the metal filament (silver on copper or gold on silver, etc.). These observations would also help us to identify the method of manufacture of the filament (beaten and cut or cast, drawn and rolled) and to determine the extent of deterioration. The energy dispersive X-ray fluorescence spectrometry (EDXRF), being a non-destructive technique, was used to give semiquantitative analysis of metal contents using 'No-standard method.' The matrix corrections were also applied to obtain accurate relative percentage. The wrapping width and thickness of all the metal threads were measured directly in SEM with its cursor.

### Results and Discussion

Ten samples were examined with optical microscope, SEM, and EDAX; the results are given in Tables I and II. Sample M1 was slightly corroded with light black colored patches containing 82% silver and 11.2% gold on the outer metal surface along with sulphur, chloride and silica. The lower layer also contained silver 82.15% and gold 12.03%. Its cross section was elliptical with clear round edges. This metal wrapping was on yellow silk core. The analysis ratios were (Ag:Au) 7.2:1 and 6.8:1 on upper and lower surface, respectively. Several points were analysed and ratios were between these values. The edges of the metal strip were smooth and no cracks were observed. This confirms that the metal thread was cast drawn and not beaten and cut. SEM examination of sample M2 showed no corrosion on the surface and that the core was silk thread. The EDXRF results showed silver:gold ratio 2.6:1 on the upper surface and 2.64:1 on the lower surface with chloride and silica in traces. This also seemed cast and drawn as the cross section was clearly elliptical. The wrapping width was 0.25 to 0.35 mm and thickness was uniformly about 3–4  $\mu\text{m}$  throughout the length of the specimen. Sample M2A was similar to M2 except that three metal threads analyzed collectively gave the silver to gold ratio as 2.2:1; copper, chloride, and silica appeared as traces. When examined by optical microscope a shiny yellow surface with no corrosion layer was seen. The presence of copper may be noted in bulk analysis which was otherwise found absent in M2.

In the case of M3, a black surface was observed under optical microscope. The metal surface was fragile, hence it was mounted on stub with great difficulty. The core of the metal thread was silk and loss of metal was seen on the upper surface. The external surface gave 90.6% silver and 5.21% sulphur while interior surface gave 86.2% silver and 7.2% sulphur. Silica, chloride and iron were also present in minor percentages. The corrosion product on the upper surface was identified as silver sulphide ( $\text{Ag}_2\text{S}$ ) by X-ray diffraction. No gold content was found on either side. The sulphur compounds liberated from silk thread may form metal sulphides which is responsible for characteristic blackening of thread (11).

Sample M3A had less blackening as compared to M3. The edges were evenly finished with core as silk thread. The EDXRF analysis gave fairly high percentage of silver (86.2%) with some iron, copper, sulphur, silica and chloride. The upper layer was slightly rubbed to remove corrosion layer and point analysis gave more than 90% silver and about 2% copper. The silk core fibre was analysed

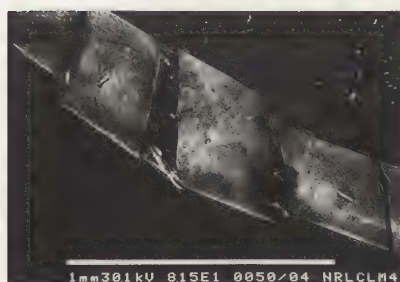


Figure 1. SEM micrograph of metal thread, sample M4 showing smooth edges without cracks. Magnification 81 $\times$ , scale bar 1 mm.



Figure 1a. Gold specific X-ray picture of figure 1.

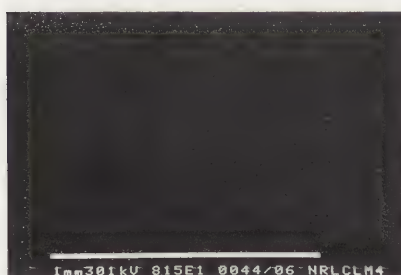


Figure 1b. Silver specific X-ray picture of figure 1.

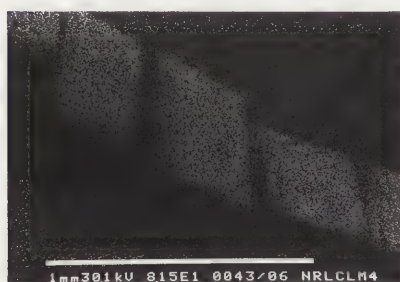


Figure 2. Scanning electron photomicrograph of the portion of sample M4 showing longitudinal striations on the inner surface may be due to flattening. Magnification 326 $\times$ , scale bar 0.1 mm.

Table I. Description of samples.

Sample no.	Specimen size	Core	Wrapping	Cross section of the wrapping
M1	3–4 mm	Silk thread	S-twist, light black colour, golden appearance, outer surface corroded, smooth edged; wrapping width: 0.2 mm, thickness: 4–5 $\mu$ m.	Elliptical
M2 & M2A	3–5 mm	Silk thread	S-twist, shining yellowish surface, no corrosion; wrapping width: 0.25–0.35 mm, thickness: 3–4 $\mu$ m.	Elliptical
M4, M4A & M4B	2–4 mm	Silk thread	S-twist, shining yellow, gold-silvery metallic appearance, smooth edged, no cracks and evenly finished; wrapping width: 0.3–0.4 mm, thickness: 6–8 $\mu$ m.	Elliptical
M5	4–5 mm	Silk thread	No metal strip, fully corroded.	—
M9	3–5 mm	Silk thread	Metal strip broken, blackish layer, heavily corroded; wrapping width: 0.31–0.4 mm.	—

and the result showed that aluminum, silica, potassium, sulphur, chloride, silver and iron were present. This also confirmed that corroded silver grains were entrapped in the fibre core.

In sample M4, the core was yellow silk thread and upper surface of metal was shiny gold and silvery in appearance, having wrapping width 0.3 to 0.4 mm and thickness varied from 6 to 8  $\mu$ m. Both the edges of metal thread strip were smooth and no cracks or cuts were observed (See fig. 1), which shows that the metal strip was drawn and cast but not cut from any foil. The longitudinal striations that were seen clearly on the lower surface (See fig. 2) also confirm drawing technology. This also shows that wire might have flattened with either power driven machine or highly skilled craftsmen. The EDXRF results showed that the exterior and interior of the metal strip were of similar composition, having silver 67.54% and 63.4% respectively along with gold 31.68% and 32.6%. The slight variation may be due to surface enrichment. Both sides of metal strip had similar composition within experimental uncertainties, suggesting that for this sample the manufacturing method was not such as to gild on one side preferentially but this was a case of fusion of coppered silver with gold leaf wrapping at a temperature about 1000°C as had been the practice during 16th–17th century (12). This may be an example of best quality of Jari thread used for decorating the prestigious tents. For more clear presentation of gold and silver distribution, the element specific X-ray radiations were photo-



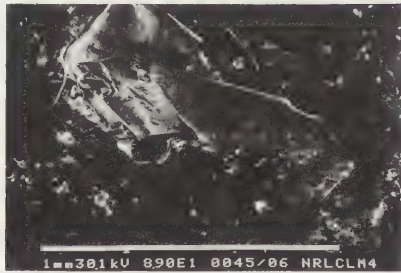


Figure 3. SEM micrograph of the small part of sample M4 showing morphology of inner and outer surfaces. Magnification 89×, scale bar 1 mm.

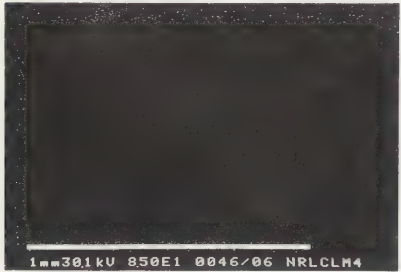


Figure 3a. Gold specific X-ray picture of figure 3 showing the gold on the upper and lower surfaces.

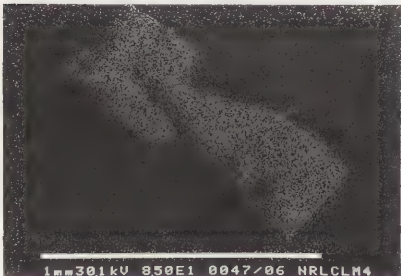


Figure 3b. Silver specific X-ray picture of figure 3 showing presence of silver on the upper and lower surfaces.

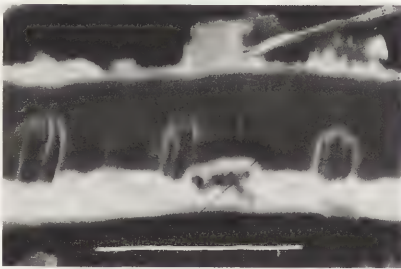


Figure 4. SEM micrograph showing cross sectional details of the sample M4. Upper and lower layers containing gold and silver while middle layer having only 97% silver. Magnification 4000×, scale 10 μm.

Table II. Elemental composition (in percentages) of samples.

Sample no.	Silver	Gold	Copper	Sulphur	Silicon	Chloride	Iron	Alu-minium
M1a	82.0	11.2	1.26	4.65	tr	tr	—	—
M1b	82.15	12.03	tr	—	tr	5.81	—	—
M2a	69.78	26.90	—	—	0.22	2.64	—	—
M2b	71.52	27.01	—	—	0.42	1.04	—	—
M2 bulk	67.45	30.60	1.08	—	0.22	0.74	—	—
M3a	90.65	—	—	5.20	tr	tr	tr	—
M3b	86.21	—	tr	7.20	tr	tr	—	—
M4a	67.54	31.68	0.71	—	—	—	—	—
M4b	63.39	32.64	0.64	—	tr	tr	—	—
M4 bulk	68.14	28.51	1.22	—	tr	tr	—	—
M5	4.98	—	—	6.19	33.55	40.70	0.21	14.37
M9a	81.88	3.71	—	7.76	0.60	5.63	—	0.42
M9b	84.63	—	0.69	7.21	0.57	5.43	0.31	1.16

a = exterior metal surface; b = interior metal surface; tr = elements present ( $\leq 2\%$ ); — = elements not found.

graphed (See figs. 3, 4); the results were also reproducible in smaller samples (See figs. 5–7). These figures also indicated the presence of gold and silver on either side. At higher magnification corrosion patches were seen as holes indicating loss of metals at some places. Some bristle-type particles seen at 1400× were thought to be silicious material but EDXRF analysis showed 72.1% silver, 25.56% gold, and 2.1% silica. No copper was found on these bristles.

As discussed above, the metal strip was fabricated with silver and gold but to see whether gold and silver is uniformly distributed along the thickness of the strip or the concentration of gold and silver varies in different layers, the sample M4 was cross sectioned and viewed in SEM (See fig. 8). This showed that the upper and lower layer were distinct, leaving an inner core with different contrast. The thickness of gold layer on outer and inner sides was about 2–3 μm and the middle silver core was 6–8 μm. The determination of elemental composition from point to point along a line, as shown in Figure 8, on the cross-section (See fig. 9) gave data to the representation of silver, gold and copper concentration profile. The middle point of the metal strip contained 97% silver but gold was absent while upper and lower layers contained silver and gold in the ratios, 2.08:1 and 1.94:1, respectively. About 1% copper was found throughout the line of the cross section. This indicated that first, a pure silver bar with about 1% copper was prepared and then gold leaf was wrapped prior to fusion. This was possible only when upper and lower layers were fused with silver bar with silver gold ratio, 2:1. This confirmed the method of wire manufacturing/drawing technique described in the census monograph (3). These could also help to distinguish the type of manufacturing technique (plating by heating, soldering, etc.) from other techniques. It is reported that copper at the rate of 10 gm/kg of silver is added at the time of melting to reduce the brittleness of silver (12). This copper silver ratio was confirmed by the presence of 1% copper in the sample M4. It was further confirmed by analysing the sample M4, originally prepared for SEM-EDAX by Atomic absorption spectrometry and 0.86% copper was found.

No metal was observed in sample M5 but the core was silk thread and showed the presence of aluminum, silica, sulphur and chloride in EDXRF analysis. In sample M9 the metal strip was broken with corroded blackish layer and silvery appearance with tarnished areas. The wrapping thickness was 0.3 to 0.4 mm and thickness varied as edges were not sharp because of corrosion. Exterior metal surface gave Ag: Au ratio as 22.1:1 with some sulphur (7.76%), silica (0.60), chloride (5.63) and aluminum (0.42). The interior metal surface showed Ag 84.63% but gold was absent. Other elements include chloride, copper, silica, iron, aluminum and sulphur.

From the above study, all the 10 samples can be categorized in to the following

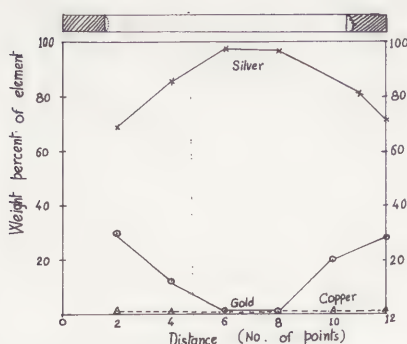


Figure 5. Silver, gold and copper concentration profile of the metal thread, M4, as represented in figure 4. The elements are detected from point to point along the line as shown in figure 4.

groups: (a) samples containing silver and gold (M1, M2, M2A, M4, M4B and M4A, M9); (b) samples containing silver only (M3, M3A, and M5).

Metals from Indian textiles of the 18th and 19th centuries were also examined by Indictor and Bisht (7). They have concluded that composition of gold rarely exceeded 10% of silver and gold total except in one case of sumptuous textile, in 19th-century brocade Ordhani. In our study sample M1, M2, M2A, M4, M4B showed more than 10% of gold in silver and gold alloy. This showed the signs of prosperity during the period when the then rulers used the tents.

### Conclusion

The sample size (2–3 mm) is sufficient to give relevant information on metal content and fabrication technology. The metal threads are wound around silk core and have an “s” twist with wrapping width varying 0.2 to 0.5 mm and thickness 3 to 10  $\mu\text{m}$ . All samples are cast, drawn and hammered except M5, as cross sections show sharp elliptical shape and edges are evenly finished. Longitudinal striations especially in M4, show that the wires are flattened either with power driven machine or highly skilled craftsmen. This leads to the conclusion that texture can also help in understanding technology. Cross section of metal thread (M4) shows no space between gold/Ag boundary and silver layer confirming complete fusion of gold leaf over silver bar. The EDX analysis gave centre core point analysis or 97% silver and about 1% gold and copper each while both the boundaries show almost similar Ag/Au ratio with about 1% copper. This confirms alloy formation surrounding the silver thread and manufacturing technique of drawing as described in the literature. Patches of corrosion and loss of metals are more pronounced where only silver threads are present. One of the black portions of metal thread was taken for XRD analysis. The result confirms the corrosion product as silver sulphide.

### Acknowledgements

The authors would like to express their gratitude to the authorities at the Mehrangarh Fort Museum, Jodhpur, Rajasthan, India for samples.

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## Abstract

The principal constituents of wax seals from parchment documents from the 13th to 17th centuries were analyzed by infrared spectroscopy, gas chromatography/mass spectrometry, and X-ray fluorescence spectrometry. Many of the data obtained can be used to distinguish the origin of the seals and create a database for Spanish sigillographic holdings.

## Keywords

Wax-seal, infrared spectroscopy, gas chromatography, mass spectrometry, X-ray fluorescence spectrometry

## The Creation of a Database for Wax Seals from Parchment Documents using the Results of Chemical Analysis

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## Introduction

The study of wax seals by chemical means is a part of a large project achieved at the Instituto de Conservación y Restauración de Bienes Culturales. This ambitious project includes the following:

- Study of the macroscopic characteristics of the seals, attending principally to the shape, colour, fillings, figures, and general state of conservation.
- Development of a methodology for analyzing the seal (wax + resin + pigments + inorganic charges) and textile attachment (fibres and dyestuffs). Once these analyses are performed, we will try to determine the craftsmen of the seal, and possible implications in documental and conservation data.
- The establishment of a standard process for conservation of the sigillographic collections, including the search for new materials to replace those currently used, in order to improve compatibility with the original components.
- The control and pursuit of the conservation processes performed over several years to test their efficiency.
- And finally, the creation of a database of all these data, to be published within two or three years, that would be accessible to all archives worldwide that have sigillographic collections.

This paper deals only with the results of the chemical analysis experiments, improving the findings of the last paper published in this area, and with the establishment of the principal lines of the conservation procedure (1).

## Description of the materials analyzed

The objects are wax or wax-resin made seals of different colours: white, yellow, brown, green and red (See fig. 1). The objects are from the following State Archives: Archivo Histórico Nacional, Archivo General de Simancas, Chancillería de Valladolid, and Archivo Histórico Provincial de Teruel. The objects comprise royal, council, ecclesiastic, and nobility seals; the social level of the owner influences the materials used for the manufacture. The composition of the organic matrix also varies regularly with chronological bases.

Although more than 200 seals have been investigated, only the most relevant seals will be discussed.

## State of the art in the sigillographic project

The methodology for the analysis of the chemical composition of wax seals has been established; the results obtained thus far have enabled us to reach some conclusions and design a general conservation process.

This process of conservation begins by cleaning the surfaces using a non-ionic detergent, and rinsing with deionized water. Once the seal is clean, it is graphically documented, such as for the macroscopic data listed above. To join the broken pieces of the seal, we have developed a melting procedure using hot stitches to hold the separated fragments. This approach was used rather than using classic metallic or wooden pieces that could produce significant damage or future cracks in the seal. To fill the gaps, a semi-synthetic coloured wax was used to differentiate between the original and restored areas. The detailed conservation procedure, including the materials used, will be detailed in a another paper.

## Experimental

Fourier-transform infrared (FTIR) analysis was performed using a Bio-Rad FTS-7 spectrophotometer with  $8\text{ cm}^{-1}$  resolution scanning on a melted film between KBr plates, within an interval of  $400\text{--}4400\text{ cm}^{-1}$ .

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Figure 1. Wax seal before (a) and after (b) restoration.

Gas chromatography (GC) was performed in a Perkin Elmer 8600 gas chromatograph with a split/splitless injector using a split ratio of 60/1. The column was a HP1 (Hewlett Packard) with a program of 180°C (initial temperature), with a ramp rate of 5°C/minute until 300°C was reached (final temperature), and maintaining this temperature for 40 minutes. The flow was 0.7 ml/minute. Two detectors were used. For making quantitative measurements, a FID (flame ionization detector) was employed. An ion trap detector (Finnigan type) was used to obtain mass chromatograms. Samples (0.02–0.5 mg) were derivatized by adding 50  $\mu$ l of benzene and 5  $\mu$ l of MethPrep® II (0.2 N methanolic solution of trifluoromethylphenyl trimethyl ammonium hydroxide, Alltech Associates), and heating at 80°C in a sealed tube for 15 minutes.

Heavy element analysis of pigments was determined by X-ray fluorescence spectroscopy using a Kevex XRF 0700 apparatus.

### Results and discussion

In order to study the organic materials, an initial spectrum of FTIR indicates the most probable composition of the wax seal. Although this is not a good technique to detect small quantities of terpenic resins in wax or to differentiate among classes of wax or resins, it can be used also to show the presence of charges, i.e., calcium carbonate, sodium carbonate, or silicates. Unfortunately, we have not yet been able to detect them, probably because they are present in very small proportions. Alternatively, these compounds may be difficult to detect due to the chemical reactions that some of them undergo (i.e., carbonates) with the acidic compounds present in resins and waxes.

The second step is to perform a gas chromatography/mass spectroscopy (GC/MS) analysis of a very small sample of the wax seal, to determine the class of wax and resin (if present), and the approximate relative proportion of each component. This parameter is used for comparison among samples.

Finally, a heavy element analysis was performed using X-ray fluorescence (XRF) to determine the pigments present.

### Organic analysis

FTIR analysis indicated the presence of wax in all cases. Only in the seals where a high proportion of terpenic resin is present was a change in the spectrum appearance observed. This change can be described as a broadening of carbonyl stretching band at approximately 1730  $\text{cm}^{-1}$ , and an increase of complexity in the 1000–1500  $\text{cm}^{-1}$  region. Sometimes a decrease of resolution and relative absorbance (with respect to carbonyl stretching band) of the doublet at 720  $\text{cm}^{-1}$  was observed (See fig. 2).

We have not found evidence of the presence of inorganic charges in the samples studied.

Gas chromatograms of two of the samples are shown in Figure 3. Acids were analyzed as their methyl esters. The identity of the compounds studied was determined by their mass spectra and their relative retention time. In all cases, comparisons were made with known compounds, with the exception of terpenic compounds, whose mass spectra were compared with the those previously described (2). The calculation of relative amounts of some compounds was effected by means of the total area found, without response factor determination.

The presence of beeswax can be ascertained by taking the prevalence of C27 (heptacosane) into account (with respect to the rest of hydrocarbons); also, all of them had odd carbon numbers (3).

It is apparently correct to suspect the presence of coniferous resins, i.e., pine resin (where present), because the appearance of dehydro- and 7-oxo-dehydroabietic acids, and lesser amounts of abietic,  $\Delta$ -8-pimaric, and sandaracopimaric acids (2).

The first conclusion that can be drawn is that a GC/MS system is the most



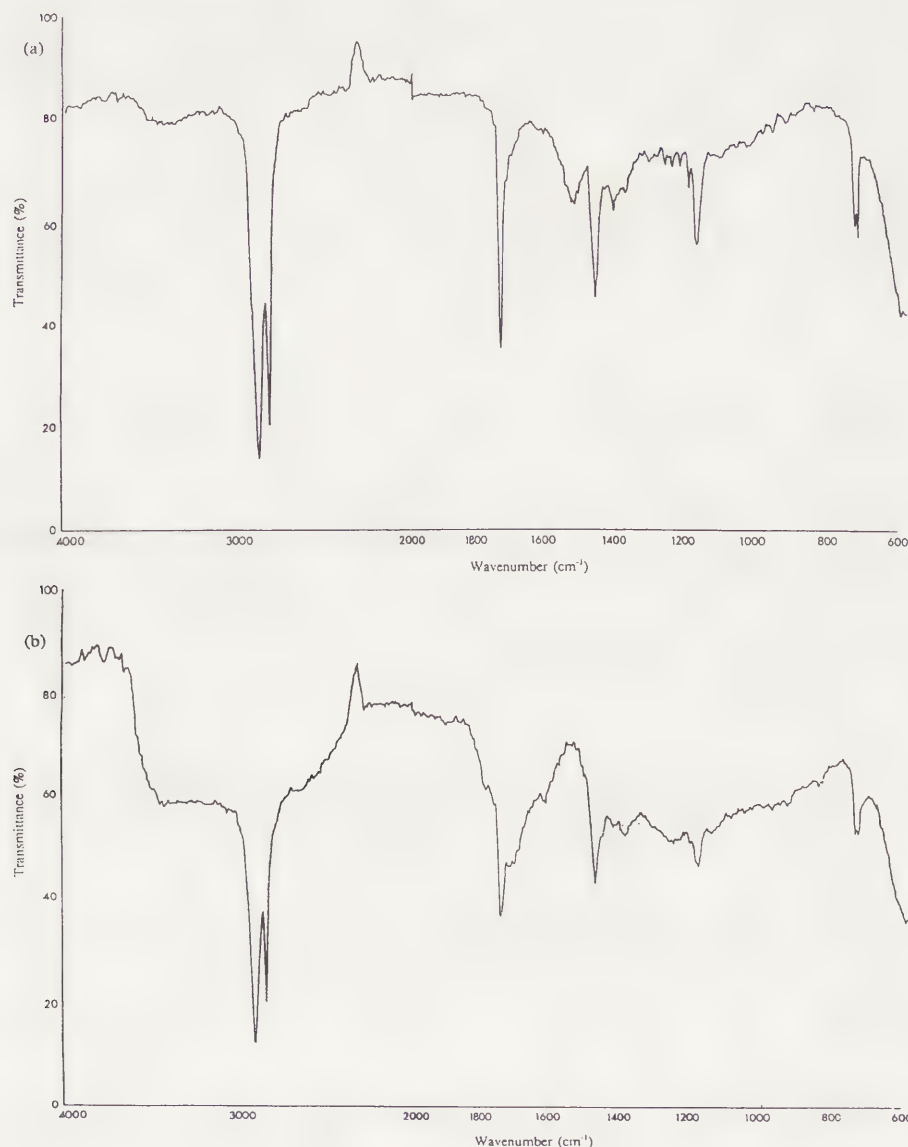


Figure 2. Infrared spectra of the samples (KBr pellet) showing the characteristic bands of (a) beeswax and (b) beeswax and terpenic resin.

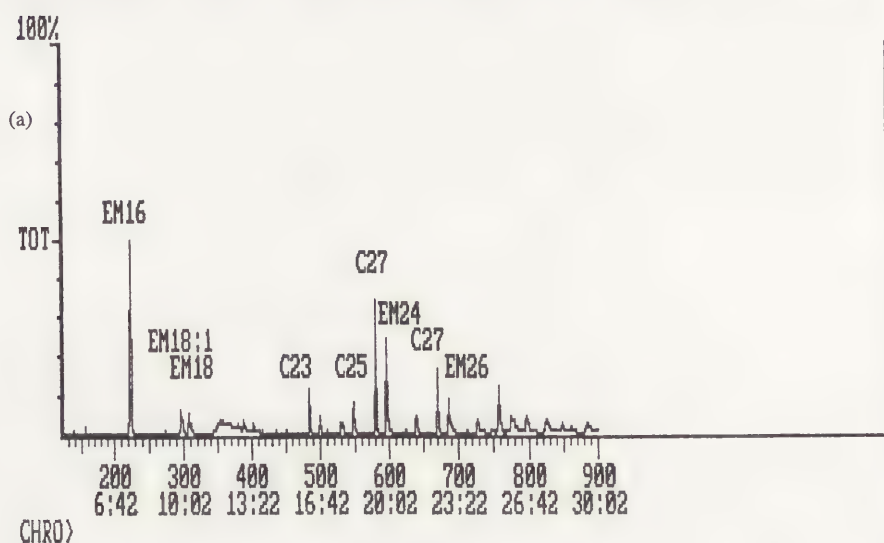
suitable technique for analyzing trace amounts of terpenes in the presence of larger quantities of other compounds, in comparison to some of the other instrumental techniques used in the past for this application (4).

The results of these analyses in some of the more relevant samples are summarized in Table I. We found traces of the terpenic compounds described above in seals dating from 1292. However, the amount of resin increases in seals made more recently. Also, other resins (apart from colophony) could be found, as for example in the seal of Felipe IV (17th century) where Venice Turpentine could be found. This presence of this resin was deduced by the presence of larixol and larixyl acetate, as well as the terpenic acids described above (2). The presence of this resin caused the partial melting of this seal when exposed to high temperatures during the summer in the workshop (30–32°C).

#### Heavy element analysis

The results of analyzing any coloured seals by X-ray fluorescence are summarized in Table II. The pigments used in the red seals were vermilion (cinnabar), lead-red, or mixtures of both. It appears that most Spanish royal seals were made using pure vermilion. In contrast, almost all private, council, and ecclesiastic seals are made with lead red, alone or mixed with vermilion. Green seals were made with copper pigments, probably copper resinate; these pigments were added or formed while elaborating the melted matrix.

Chromatogram A:SE9770 Acquired: Jun-03-1991 13:53:41  
 Comment: SELLO DE CERA 9770 + METH PREP 180 5C/MIN 300 40MIN  
 Scan Range: 121 - 900 Scan: 121 Int = 99519 @ 4:05 100% = 14094308



Chromatogram A:SE9733 Acquired: Jun-04-1991 09:02:25  
 Comment: SELLO DE CERA 9733 + METH PREP 180 5C/MIN 300 40MIN  
 Scan Range: 121 - 900 Scan: 121 Int = 42904 @ 4:05 100% = 1901172

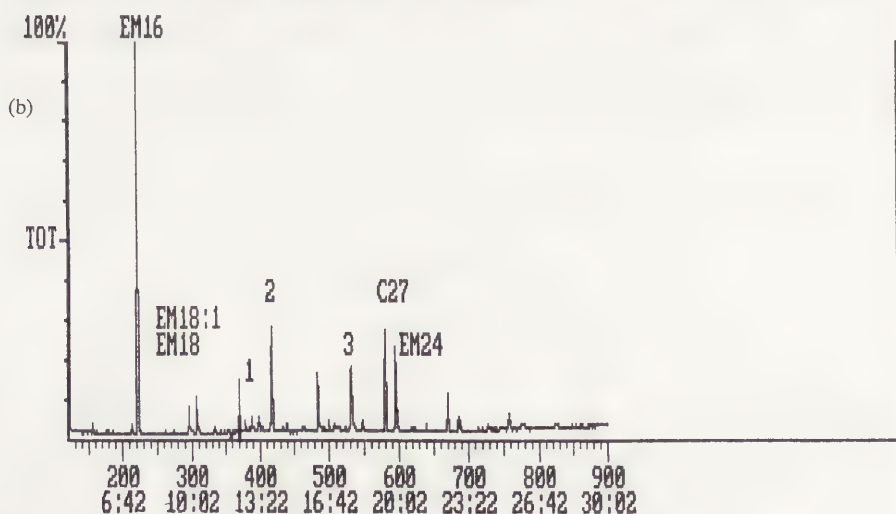


Figure 3. Total Ion Current reconstructed gas chromatogram with some of the relevant peaks. (a) Bees wax: EM16 methyl palmitate, EM18:1 methyl oleate, EM18 methyl stearate and C27 heptacosane; (b) Bees wax and colophony resin: 1) methyl isopimarate, 2) methyl dehydroabietate, 3) methyl 7-oxo-dehydroabietate and EM24 methyl eicosatetrate.

It is difficult to explain the presence of yellow and brown colours in seals. We are of the opinion that inorganic pigments are the cause of the yellow color in the seals; it is more probable that an unidentified yellow dyestuff was used. The presence of brown colours could be due to the use of a less refined beeswax, or to the decomposition of copper-containing green pigments, as traces of copper were detected in some of the brown seals.

### Conclusions

FTIR, GC/MS, and XRF techniques provide useful information about the constituent materials of wax seals, and pigment analysis may allow researchers to differentiate the social origins of seals. An increase in the amount of terpenic resin has been observed in seals made after the second half of the 16th century,



Table I. Results of the comparison of the organic analysis performed on relevant samples of wax seals.

Chronology	Belongs to	Colour	Beeswax	Colophony	VT
1250	Gonzalo Díaz	brown	++	—	—
1256	Pelayo Pérez, Maestre de la Orden de Santiago	white	++	—	—
1259	Pelayo Pérez	white	++	—	—
1284	Pedro Núñez, Maestre de la Orden del Temple	yellow	++	—	—
1292	Andrés de Liñán	white	++	—	—
1324–1329	Domingo, Patriarca de Grado	red	++	(+)	—
1324–1329	Guillermo, Obispo de Segovia	red	++	(+)	—
1324–1329	Bonifacio, Obispo de Solci	red	++	+	—
1324–1329	Estaban, Obispo de Luebeck	red	++	(+)	—
1556	Felipe II, Rey de España	red	++	+	—
1621–1665	Felipe IV	red	+	+	—
1621–1665	Felipe IV	red	+	+	—
1621–1665	Felipe IV	red	+	+	+
1660–1685	Carlos II, Rey de Inglaterra	yellow	+	+	—

Key: ++ = major substance; + = present; (+) = traces; — = absent; VT = Venice turpentine.

Table II. Results of the heavy element analysis (by XRF) on samples of coloured wax seals.

Chronology	Belongs to	Colour	Element	Pigment
1255	Jaime I King of Aragón	Black	—	?
1258	Juan I King of Aragón	Red	Hg	Cinnabar
1284	Pedro Nuñez, Maestre de la Orden del Temple	Yellow	—	?
1292	Pascual Domínguez, Bishop of Pamplona	Red	Hg	Cinnabar
1324–1329	Domingo, Patriarca de Grado	Red	Hg, Pb	Cinnabar + Lead red
1324–1329	Francisco, Bishop of Perusa	Red	Pb	Lead red
1324–1329	Guillermo, Bishop of Segovia	Red	Pb	Lead red
1324–1329	Gerardo, Bishop of Gernia	Red	Pb, Hg↓	Lead red + Cinnabar↓
1366	Pedro IV, King of Aragón	Red	Hg	Cinnabar
1420	Juana II, Queen of Sicily	Red	Hg, Pb	Cinnabar + Lead red
1549	Carlos I, King of Spain	Red	Hg	Cinnabar
1512	Enrique VIII, King of England	Green	Cu	Copper resin-ate
1621–1665	Felipe IV, King of Spain	Red	Hg	Cinnabar

but small quantities can be detected in seals from the late 13th century to the first half of the 16th century. Knowledge about the materials used to fabricate the seals can be obtained using both documentary evidence and experimental data.

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## Abstract

A program of color measurement was undertaken as part of a project to document and conserve the wall paintings in the tomb of Nefertari, located in Luxor, Egypt. The color data showed that cleaning resulted in increased saturation of the colors of the paintings, with no measurable change in hue for most colors. Reds, blues and greens took on deeper tones after treatment, yellows became brighter and more vivid, and blacks appeared darker. Other information obtained from the data related the color of painted areas with the nature of the pigmentation present. In order to aid in the interpretation of the color measurement data from the wall paintings, the performance of the Minolta Chroma Meter CR-121 was fully evaluated. The degree of precision, accuracy and stability exhibited by the CR-121 indicates that the instrument is suitable for projects in which color changes are to be evaluated.

## Keywords

Nefertari, color measurement, wall paintings, Chroma Meter, CIELAB

## Color Measurement of the Wall Paintings in the Tomb of Nefertari

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## Introduction

Since its discovery in 1904 by the archaeologist Schiaparelli, the tomb of Nefertari has occupied a significant place in the cultural heritage of Egypt. Located in the Valley of the Queens in Luxor, the tomb is renowned for the vividness of color and historical significance of its wall paintings that depict Queen Nefertari in various religious and funerary scenes. Unfortunately, the tomb has been closed to the public ever since its discovery because of the precarious state of the wall paintings, which have suffered the effects of salt crystallization.

In September of 1985, the Egyptian Antiquities Organization and the Getty Conservation Institute initiated a joint program to preserve the wall paintings. To accomplish this task, a multidisciplinary team from around the world was assembled to study the tomb, assess the damage to the wall paintings and implement the conservation treatment. As a part of the study of the wall paintings, a program of color measurement was undertaken in order to provide supplementary documentation for the conservation procedure [1]. Upon careful examination, it was clear that removal of surface dirt and grime would significantly enhance the appearance of the colors of the wall paintings. The ideal treatment procedure would leave the hues of the paintings unaffected, but enhance the brightness and saturation of the colors.

Thus, it was important to measure and record the colors of the wall paintings prior to treatment, and to use this record to evaluate the proposed treatment method. Several methods exist for color documentation, such as color photography, Munsell color matching, and instrumental measurement; each technique has certain advantages and disadvantages. Color photography can rapidly document large areas of wall paintings, but the photographic color record is notoriously inaccurate and impermanent.

A set of colored reference chips categorized by hue, value and chroma (HVC) is the basis of the Munsell system of color notation [2]. The hue, value and chroma of each chip is described by an alphanumeric label that uses the convention H V/C. In Munsell hue terminology, R signifies reds, Y = yellows, G = greens, B = blues, P = purples, N = neutrals. Intermediate hues are assigned two-letter combinations, such as YR for orange, GY for greenish yellow, RP for reddish purple and so on. In addition to the letter designation, a numeric prefix expresses the shade (for example, 2.5GB is greener than 10GB). Munsell value increases with lightness (for example, a light orange has a value of 7, whereas 2 indicates a darker orange). Chroma increases with saturation (an orange with a chroma of 2 appears much paler than an orange with a chroma of 16). Thus, using Munsell terminology to describe a hypothetical bright orange color, the complete designation might be 7.5YR 7/16.

In a set of Munsell chips, hue number is incremented every 2.5 units, value every one unit, and chroma every two units. An interesting feature of the Munsell system can be observed by placing the colored reference chips in a three-dimensional array, with hues arranged in a circle (R, Y, G, B, P around the perimeter, and N in the center), value increasing in the vertical direction, and chroma increasing horizontally. The system was designed so that, to an observer with appropriate lighting conditions, the difference in color between any two neighboring chips is roughly equivalent.

The Munsell system can be used to describe the colors of objects by finding the chip closest in color to the object's color. Although simple in concept, the procedure can be tedious, and eyestrain can result. Furthermore, for accurate



results the lighting conditions must be well-controlled, and the acuity of the viewer's color perception is crucial. Even under ideal conditions, rather broad tolerance limits result due to the wide spacing of adjacent Munsell chips. Ultimately, the decision was made to use a color measuring device to record the colors of the Nefertari wall paintings, and to calculate color differences brought about by the cleaning procedure.

Two campaigns were made to Luxor, during which time the colors of the wall paintings were recorded. The first campaign occurred during September of 1986, the results of which were discussed in the first progress report [1]. After this campaign, several improvements were made in the calibration procedure, as well as the method of data expression. These improvements were implemented during the second campaign, in May of 1987. The final project report, scheduled for publication in 1993, is the basis for the present article [3].

### Experimental Details

A Minolta Chroma Meter CR-121 was the instrument chosen to record the color data. The instrument is a portable, battery-operated, tristimulus colorimeter ideally suited for field projects and museum studies [1]. The detachable measuring head has a 3 mm diameter aperture, and a built-in xenon flash. Like other tristimulus colorimeters, the Chroma Meter CR-121 employs three filters which approximate the response of the 1931 CIE standard observer. This feature permits the instrumental design to be greatly simplified (as compared to a spectrophotometer), at the expense of accuracy.

The instrumental design allows the device to be used in contact with objects with only minor modifications required. A small piece of Goretek was applied to the end of the instrument to prevent damage to the wall paintings during measurement (see Figure 1). The instrument was calibrated against a white ceramic tile prior to use.

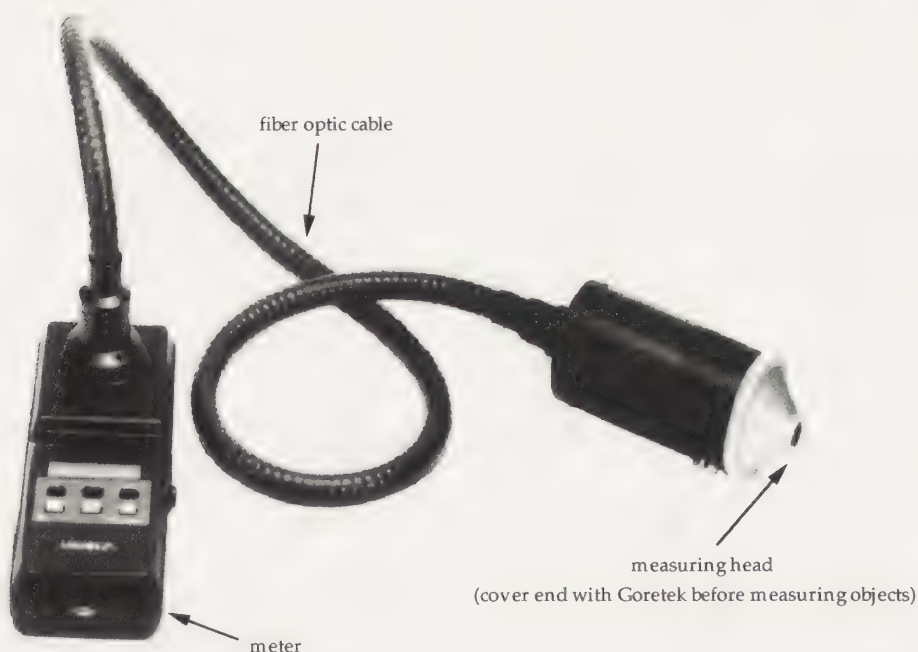


Figure 1: Photograph of Minolta Chroma Meter CR-100 (similar to CR-121, but with larger measuring area). Courtesy of Minolta Corporation.

Making color measurements of the wall paintings involved the following procedure. The locations for measurement in the tomb, selected to represent the various states of preservation of the wall paintings, ranged from well-preserved to near total detachment of the painted plaster. Measurement locations were recorded photographically with Polaroid film, and cross-referenced with the floor plan for indexing purposes.

The majority of the painted surfaces in the tomb were prepared for measurement

by light dusting with a squirrel hair brush, under a gentle stream of air produced by a rubber bulb syringe. This procedure removed surface dust that had settled on the paintings which could affect the quality and reproducibility of the data. For those areas where the proposed conservation treatment method was evaluated, color measurements were made without prior dusting.

Because of inhomogeneity of the colors of the wall paintings, irregularity of the painted surfaces, and difficulty in precisely locating the measuring head at each desired point, it was thought that single measurements at each location would yield misleading results. Thus, it was decided to select three locations within each colored area, each of which was measured three times. The variation in coloration of each area could be determined (if desired) from the data at the three measured areas. Measurement reproducibility could be calculated from the three measurements at each area (as discussed below).

Measurement data originally expressed in chromaticity coordinates ( $Yxy$ ) were converted into CIELAB notation ( $L^*a^*b^*$ ) for data evaluation [2]. The CIELAB system of color notation utilizes the principle of opposing colors, as shown in Figure 2. Lightness is defined as  $L^*$ , and hue is expressed in terms of  $a^*$  and  $b^*$ . Positive values of  $a^*$  refer to red hues, and negative values to green hues. Similarly, yellows have positive  $b^*$  values, and blues have negative values. Chroma,  $C^*$ , is defined in CIELAB color space as [2]:

$$1. \quad C^* = \{(a^*)^2 + (b^*)^2\}^{(1/2)}.$$

Color data can be expressed graphically or in tabular form. Color charts, which are graphs of  $b^*$  versus  $a^*$  or  $L^*$  versus  $a^*$ , are convenient for illustrating groups of color measurement data, and for providing visual alternatives to data tables.

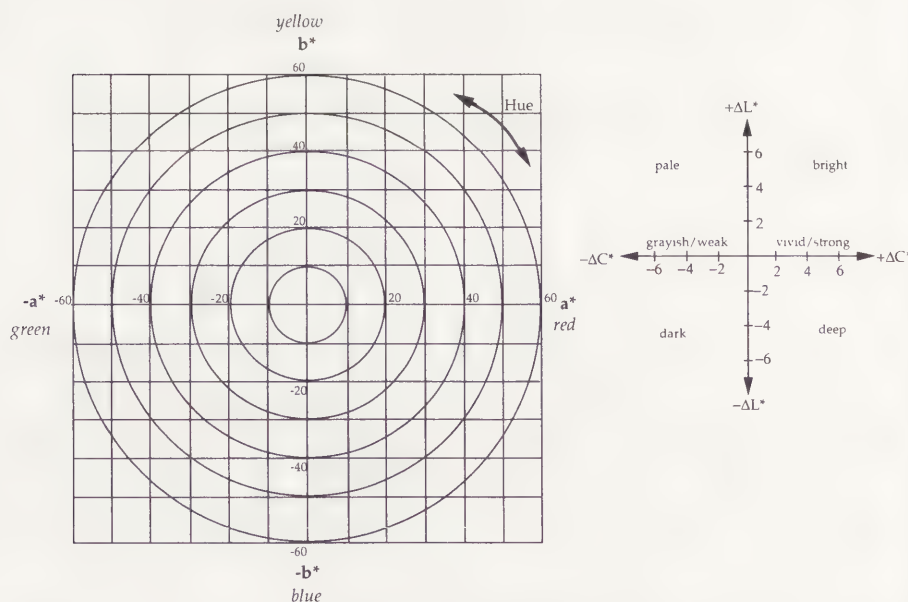


Figure 2: a)  $L^*a^*b^*$  color chart, illustrating CIELAB system of color notation; and b) Color tone chart for displaying tone differences.

Color change or color difference can easily be determined by using the CIELAB system [2]. Changes in chroma are expressed in terms of  $\Delta C^*$ , and lightness changes in terms of  $\Delta L^*$ . Color difference,  $\Delta E$ , is equal to:

$$2. \quad \Delta E = \{(\Delta L^*)^2 + (\Delta a^*)^2 + (\Delta b^*)^2\}^{(1/2)}.$$

Color charts are excellent tools for displaying color changes for small sets of data. Plots of  $\Delta L^*$  versus  $\Delta C^*$  show in which visual direction color changes occur, as displayed in Figure 2. Additionally, in graphs of  $b^*$  versus  $a^*$ , hue shifts appear as rotations about the origin, and are expressed in terms of hue angle. Thus, CIELAB color notation provides a system in which color change and absolute color can be expressed.



### Instrumental Evaluation

An important component of this and any other color monitoring program is the evaluation of the performance of the color measuring device, in this instance the Minolta Chroma Meter CR-121. Wall paintings have inherently inhomogeneous paint layers, in addition to irregular surfaces. These physical factors impact measurement reproducibility. Second, determination of color change requires that the measuring device be stable over the time period involved. Otherwise, any apparent color change would be indistinguishable from instrumental drift. And finally, although absolute accuracy is not paramount in color difference measurements, it is desirable to produce results comparable to those from a human observer using the Munsell system.

Thus, instrumental reproducibility, stability and accuracy were evaluated in order to assess the effects of each on the measurement data. Instrumental accuracy and stability were checked periodically against British Ceramic Research Association (BCRA) ceramic color standards (set CCS-II). These tiles were prepared to be uniformly colored, and stable under normal storage conditions. Reproducibility calculations were based upon the measurement data from the wall paintings (as discussed earlier), rather than the data from the CCS-II tiles.

In measurements of the tiles the CR-121 consistently yielded results accurate to within one Munsell chip of the nominal value for the entire set of tiles, as shown in Table I. This performance is comparable to that of many human observers, without the corresponding limitations (eyestrain, fatigue). This level of accuracy is acceptable for most field conservation work.

Table I. Munsell data for BCRA CCS-II tiles. Comparison of manufacturer's data to CR-121 measurement data for determination of instrumental accuracy.

BCRA tile name	Manufacturer			CR-121			$\Delta E$
	H	V	C	H	V	C	
Pale grey	2.1G	8.1	0.1	6.8GY	8.0	0.2	1.0
Mid grey	1.7G	5.4	0.1	0.9G	5.3	0.1	1.2
Deep grey	2.4GY	2.5	0.1	7.4GY	2.5	0.2	0.8
Deep pink	0.1R	3.9	6.4	1.8R	3.9	6.3	2.9
Red	8.3R	3.4	12.6	9.1R	3.4	12.4	4.0
Orange	2.8YR	6.4	13.2	3.4YR	6.2	12.9	3.5
Bright yellow	5.7Y	8.3	12.7	6.0Y	8.0	11.7	7.7
Green	3.0G	5.0	6.8	3.9G	4.8	6.1	5.1
Cyan	9.6B	4.8	8.7	0.6PB	4.7	8.7	2.2
Deep blue	8.1PB	0.8	9.4	7.6PB	0.8	7.4	8.3

Note: Munsell conversions performed by a computer program loaned to the GCI by Max Saltzman. Conversion of chromaticity data to CIELAB color difference units was made using the CIE 1976  $L^*a^*b^*$  equation and CIE 1976 color difference equation.

The stability of the CR-121 was determined by periodic measurement of the CCS-II tiles. The data in Table II, an excerpt from the stability measurements which have been collected to date, exhibit no pronounced long-term drift over the first two years, and approximately two units of drift subsequently.

It is possible to correct for long-term drift over the course of the project, and improve the accuracy of the instrument, by using linear regression analysis. The computer program which performs this correction was developed for Max Saltzman, an independent consultant, by Roy Berns and his students at the Rochester Institute of Technology [4]. Essentially, the program relies upon statistical equations to regress the measured set of tristimulus values onto the manufacturers data set. Although a complete discussion of the statistical results is inappropriate for this publication, application of the regression results improves the measurement results relative to the CCS-II tiles, thus correcting for a significant amount of the long-term drift. In other words, in the event that locations in the tomb require remeasurement at a later date, the tomb data can be corrected for instrumental drift by comparison with the reference tile measurement data.

Table II. Periodic measurement data for BCRA CCS-II tiles for evaluating instrumental stability.

Color	Date	L*	a*	b*	$\Delta E$	H	V	C
Red	9/86	35.0	50.0	42.4	ref	9.1R	3.4	12.4
	12/86	35.2	50.2	42.6	0.3	9.1R	3.4	12.5
	5/87	35.2	49.8	42.6	0.4	9.1R	3.4	12.4
	9/87	35.4	50.2	42.5	0.5	9.0R	3.4	12.5
	3/89	34.8	48.5	42.4	1.4	9.3R	3.4	12.1
	3/90	35.6	48.9	42.2	1.3	9.2R	3.5	12.2
	5/92	35.7	48.7	41.6	1.7	9.1R	3.5	12.2
Green	9/86	50.0	-31.9	12.8	ref	3.9G	4.8	6.1
	12/86	50.2	-32.3	12.7	0.5	4.0G	4.9	6.2
	5/87	50.0	-31.3	12.2	0.8	4.1G	4.8	6.0
	9/87	50.0	-31.8	12.3	0.5	4.1G	4.8	6.1
	3/89	49.0	-30.7	11.5	2.0	4.2G	4.8	5.9
	3/90	49.9	-31.1	10.9	2.0	4.6G	4.8	5.9
	5/92	49.3	-30.8	10.8	2.3	4.6G	4.8	5.9
Cyan	9/86	48.1	-9.5	-33.7	ref	0.2PB	4.7	8.6
	12/86	48.0	-9.0	-33.5	0.5	0.4PB	4.6	8.6
	5/87	48.1	-9.0	-33.6	0.5	0.4PB	4.7	8.6
	9/87	47.9	-8.5	-33.4	1.0	0.5PB	4.6	8.5
	3/89	47.1	-7.7	-33.9	2.1	0.8PB	4.6	8.6
	3/90	47.8	-7.8	-34.3	1.9	0.8PB	4.6	8.7
	5/92	47.2	-7.5	-34.3	2.3	0.9PB	4.6	8.6

Note: Munsell conversions performed by a computer program loaned to the GCI by Max Saltzman. Conversion of chromaticity data to CIELAB color difference units was made using the CIE 1976  $L^*a^*b^*$  equation and CIE 1976 color difference equation.

To provide a realistic assessment of measurement reproducibility within the tomb, the data were sorted into the five main colors: blue, green, red, yellow, and neutrals (whites and blacks). The first reading at each point was arbitrarily chosen as the reference measurement, relative to which color differences were calculated for the two remaining measurements. Color differences were expressed in terms of  $\Delta L^*$ ,  $\Delta a^*$  and  $\Delta b^*$ , and  $\Delta E$ .

The mean and standard deviation of  $\Delta L^*$ ,  $\Delta a^*$ ,  $\Delta b^*$  and  $\Delta E$  were calculated for the four primary hues, and the results are shown in Table III. The values reported

Table III. Reproducibility of wall painting measurements. Mean and relative standard deviation of triplicate readings measured at each location.

Color of wall painting	Evaluation	$\Delta L^*$	$\Delta a^*$	$\Delta b^*$	$\Delta E$
Blue	mean	0.9	0.3	0.7	1.3
	rsd	1.0	0.4	0.8	1.2
Green	mean	0.8	0.6	0.5	1.3
	rsd	1.3	0.9	0.7	1.6
Red	mean	0.7	0.6	0.6	1.2
	rsd	0.8	0.7	0.7	1.1
Yellow	mean	0.8	0.5	1.2	1.6
	rsd	0.9	0.5	1.6	1.7

in this table reflect the entire set of data; none of the readings which exceeded the three sigma limit were disregarded. The variations between measurements at single locations were found to be roughly one unit of difference for  $L^*$ ,  $a^*$ ,  $b^*$  and  $E$ , which is essentially the limit of just-perceptible color difference for most human observers. These numbers were found to be much smaller than the typical spread of data for readings taken at cleaned and uncleaned areas (discussed below). Thus, the measurement protocol using the CR-121 was shown to be suitable for determining color changes in the tomb of Nefertari.



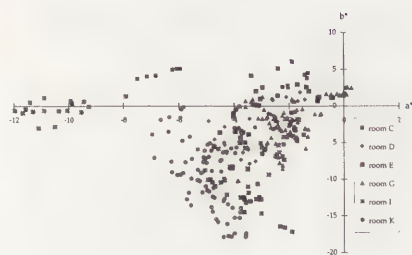


Figure 3: Color chart for blues, sorted by room, illustrating clustering of data by room.

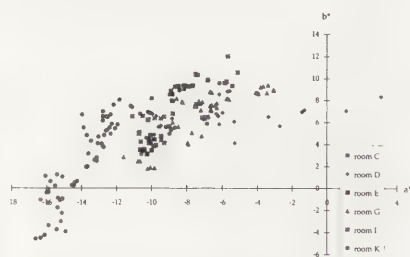


Figure 4: Color chart for greens, sorted by room, illustrating clustering of data by room.

### Summary of Color Measurement Data of the Wall Paintings

Approximately 1500 color measurements were made at 160 different locations of the wall paintings in the Tomb of Nefertari, on as many colored areas as time permitted during the second field campaign. An attempt was made to include every color and shade appearing in as many rooms of the tomb as possible.

Individual  $b^*$  versus  $a^*$  graphs for the four major colors sorted by room revealed clustering of the data for blues and greens. In Figure 3, the data for the blue areas in rooms I and K are spread over the entire region of the graph, whereas for the other rooms the data cluster near the top. For the greens, shown in Figure 4, the data for room K are located at the left side of the graph. Because the spread of the data is well outside of the reproducibility limits established earlier in this report, the clustering effect appears to be significant. Furthermore, the magnitude of this effect exceeds the variability due to the cleanliness of the painted surfaces alone.

The clustering may be caused by the nature of the pigmentation in the blues and greens, identified by polarized-light microscopy and electron microprobe analysis as the synthetic pigments Egyptian blue and Egyptian green [3]. Batch-to-batch variability of these man-made pigments may have resulted in two distinct shades of blue and green, as detected by the CR-121. This hypothesis would require additional sampling and analysis for verification. In support of this hypothesis, the mineral pigments yellow ochre, hematite, and burnt umber do not fall into any well-defined categories, but instead possess broad ranges of color.

### Effects of Cleaning on the Colors of the Wall Paintings

Before the color measurement campaign in September 1987, the efficacy of the proposed cleaning method was tested on a small section of the back wall in the main burial chamber, room K, in an area which contained blue, black, red, green, and yellow paint [3]. This area provided an excellent opportunity to determine the effect of the cleaning method on the colors.

A thorough investigation of the state of preservation of the paintings was conducted, accompanied by a study of the material history and previous restoration efforts. Laboratory analyses of pigments, binding media and coatings provided a basis for precise treatment, and confirmed hypotheses based upon visual examination [3]. The picture layer was covered with dust and an inhomogeneous gray layer, especially evident on the white background, and was most likely caused by smoke from petrol lamps used during excavations and inspections earlier this century. Surface contamination from dust was removed by a low-

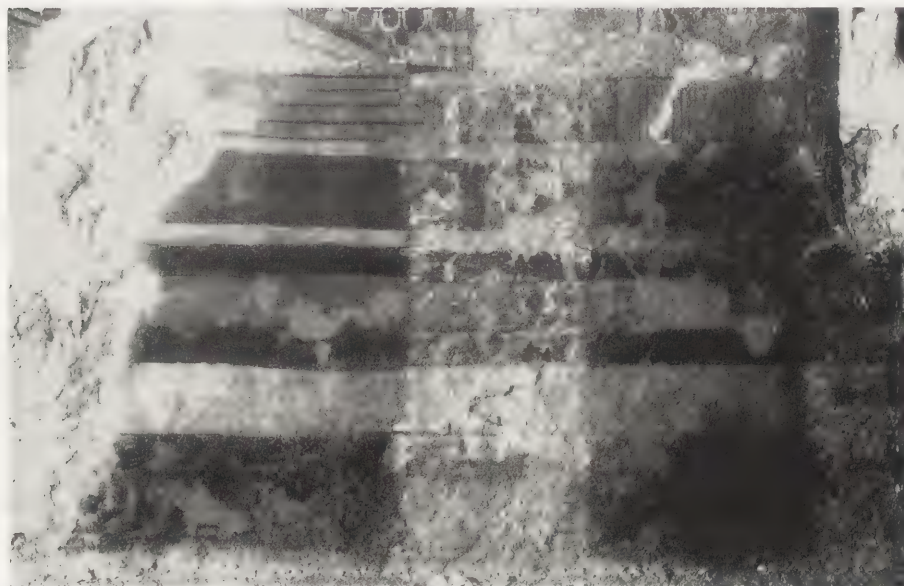


Figure 5: Photograph of cleaned and uncleaned areas in room K, north wall, west side, showing areas where cleaning procedure was evaluated.

pressure air stream, and the gray layer was removed by acetone applied with compresses [3].

Color measurements were made at each cleaned area and a nearby area that remained uncleaned. Unfortunately, it was impossible to make measurements of the original area before cleaning, because the method was undertaken in a previous campaign. However, the color data serve to illustrate the magnitude and direction of the changes resulting from cleaning. Figure 5 shows the area where the treatment method was evaluated (and also illustrates the method of recording the color measurement locations).

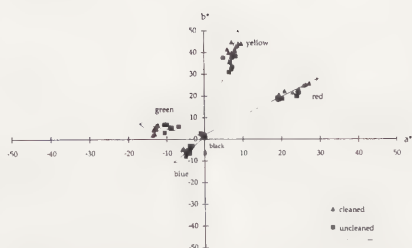


Figure 6: Color chart for cleaning test area in chamber K, showing effects of cleaning on color.

The  $b^*$  versus  $a^*$  color chart of the data, Figure 6, shows that the data for the cleaned areas lie farther from the origin than the uncleaned areas, indicating that cleaning increased the CIELAB chroma of the colors. No measurable hue shift was detected after cleaning for most colors. In Figure 6 it can be observed that, for each of the five main colors, the data for the cleaned areas cluster around a radial line extending from the origin through the data points for the uncleaned areas. If a change in hue had occurred, the set of data for the cleaned surfaces would lie off the line. The Munsell data in Table IV show that cleaning resulted in small changes in hue number for most colors. The green paint exhibited the largest change in hue number, registering a full chip of difference.

Table IV. Comparison of cleaned and uncleaned areas in Tomb of Nefertari.

Area description	CIELAB data			Munsell data		
	$L^*$	$a^*$	$b^*$	H	V	C
Cleaned black	24.3	-0.3	1.6	7.6Y	2.4	0.3
Uncleaned black	32.7	-0.6	2.1	8.9Y	3.2	0.3
Cleaned blue	32.9	-5.0	-6.1	5.0B	3.2	1.7
Uncleaned blue	39.4	-4.1	-4.6	4.8B	3.8	1.4
Cleaned green	48.5	-12.9	4.6	4.9G	4.7	2.5
Uncleaned green	51.4	-9.5	5.8	1.6G	5.0	1.9
Cleaned red	43.4	23.3	23.0	0.6YR	4.2	6.0
Uncleaned red	48.1	20.8	19.4	0.01YR	4.7	5.4
Cleaned yellow	60.5	8.0	42.5	0.4Y	5.9	6.6
Uncleaned yellow	59.3	7.2	36.0	0.2Y	5.8	5.6

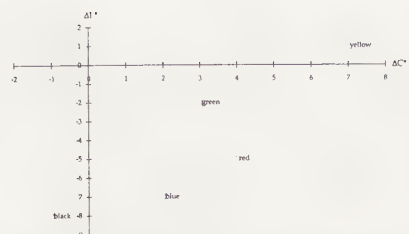


Figure 7: Color tone chart of cleaning test area, illustrating magnitude and direction of color changes after cleaning.

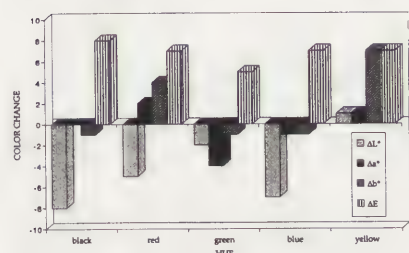


Figure 8: Bar graph of data from cleaning test area, showing magnitude of color changes due to cleaning.

The color tone chart in Figure 7 shows that reds, blues and greens became deeper after cleaning (using the terminology discussed in Figure 2), whereas yellows became brighter and more vivid, and blacks became darker. For quantitative evaluation of the magnitude of the color changes caused by the cleaning treatment, the data from the cleaned and uncleaned areas were reduced to bar graph format, shown in Figure 8. For blues and blacks the overall color change  $\Delta E$  is dominated by a decrease in lightness,  $L^*$ .  $\Delta E$  is relatively evenly divided between  $L^*$ ,  $a^*$  and  $b^*$  for reds and greens. For yellows,  $\Delta E$  is due largely to an increase in  $b^*$  (positive  $b^*$  values indicate relative yellowness). Therefore, removal of the light-colored dirt layer which covered the wall paintings returned the colors to a more saturated appearance.

## Conclusions

In summary, it has been demonstrated that the Minolta Chroma Meter CR-121 is an ideal tool for conservation purposes, especially in determining color difference. The device is easy to use, portable, and capable of measuring most colors to within one Munsell chip. A long-term, periodic evaluation of stability revealed only slight drifting at a level for which mathematical correction can be made. Furthermore, in measurements of wall paintings the data are reproducible to within one unit of color difference. In conclusion, the CR-121 is well suited for measuring the colors of the wall paintings, such as in the tomb of Nefertari.

Ultimately, the color record obtained in the second field campaign provides the



basis for future evaluations if any changes occur in the colors after treatment due to visitor impact or any other environmental influences.

### Acknowledgments

The author wishes to thank the following for their advice, assistance and direction during the course of this project: Max Saltzman, an independent consultant and expert in color technology; Frank Preusser, Associate Director, Programs, the Getty Conservation Institute; Roy Berns, Director of the Munsell Color Science laboratory, Rochester Institute of Technology; The Staff of the Industrial Meter Division of the Minolta Corporation; Mike Preston, Sales Representative of Wolff Engineering.

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## Abstract

The dimensional response of parchment to changes in relative humidity was studied using RH-step jump thermomechanical analysis, in order to determine the optimum RH conditions for storage of the Dead Sea Scrolls. The magnitude of the dimensional change that occurs on reducing the storage relative humidity is considerably smaller for degraded parchments than for modern parchment. In addition, although the half-time for establishment of water vapor equilibrium is longer for degraded parchments than for modern parchment, the absolute response time is relatively rapid. Furthermore, scroll samples, degraded modern parchment and gelatin showed little ( $<0.2\%$ ) permanent dimensional changes following RH cycling to 16% under the test conditions. This is in contrast to the 1% deformation shown by modern parchment. In conclusion, because brittleness and cockling become important factors at low RH, a reasonable compromise RH between hygric expansion stability and mechanical stability seems to be  $35 < RH < 40\%$ .

## Keywords

Dead Sea Scrolls, parchment, thermomechanical analysis, gelatin, relative humidity

## The Effects of Relative Humidity Changes on Dead Sea Scrolls Parchment Samples

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## Introduction

The Dead Sea Scrolls were discovered in caves in the Judean Desert in Israel over a period of time starting in 1947. The Scrolls were made of parchment, prepared from the unsplit skin of sheep or goats, by methods prescribed by rabbinical regulations [1]. The longer scrolls were found tightly rolled and were hard and brittle. Plenderleith [2] found that an overnight exposure to 75% relative humidity (RH) followed by a six hour exposure to 80% caused laminated scroll fragments to become limp enough to permit separation. A number of the major scrolls were able to be unrolled only after exposure to 100% RH.

Fragments and wads of parchment were also found that, when wetted, became soft and sticky. Plenderleith stated that this material disintegrated in water and he concluded that the parchment had been converted into a form of glue, the ultimate decomposition product of skin.

When unrolled, the scrolls were found to be in a partially deteriorated condition. The inner layers of the rolls, which were protected to some extent, appeared to be unaffected, whereas the outer layers and edges that had been exposed to the environment were darker and adhered tightly to each other.

Collagen, the principle component of parchment, is known to undergo hydrolytic breakdown when exposed to high humidity and low pH conditions [3]. When the breakdown becomes excessive, denaturation or the loss of the three chain helical structure occurs, with the result that the collagen is converted to gelatin.

In the case of the Dead Sea Scrolls, it is not known when the conversion occurred. Although the caves where the scrolls were found were supposedly dry, heavy rainfall does occur in the desert, hence both flooding and RH conditions approaching 100% may have occurred during this time. Thus, most of the observed degradation could have occurred in antiquity [4]. However, the conditions under which the scrolls were stored after their discovery by Bedu shepherds and before their acquisition by museum authorities have not been determined. It is quite possible that further degradation may have taken place during this time period.

Because of the brittleness of degraded parchment and the likelihood of fracture under stress, it would be logical to maintain the scrolls under a high humidity environment. However, since high humidities are known to accelerate degradation, storage at low RH should reduce the rate of collagen to gelatin conversion. To maintain the integrity and minimize further degradation of the scrolls, optimum RH storage conditions need to be defined.

In an earlier study [5], it was demonstrated that a significant increase in stress occurred when a restrained sample of contemporary, undeteriorated calfskin parchment was exposed to an RH of less than 22%. This is consistent with the theory that at a low water content, water bound within the helical chain is lost, causing the chains to shrink [6]. These results do not necessarily apply to scroll parchments, because the composition and structure of degraded parchment is quite different from that of the modern material in that gelatin is a major component and the fibrous nature of the parchment has been altered. A similar type of measurement could not be performed on scroll samples because of the small quantity of parchment available for testing and the extreme fragility of the samples.

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Accordingly, another method was used for measuring the dimensional response of Dead Sea Scroll fragments as a function of RH. The method employed a modified thermomechanical analyzer, used in a constant temperature mode, under variable RH conditions. The test procedure involved exposure of a scroll sample to atmospheres of decreasing RH in discrete steps, followed by reversal of the RH level back to the original value. Changes in sample thickness were recorded continuously.

### Description of Test Instrument

Thermomechanical analysis (TMA) is a technique in which dimensional changes of small samples can be accurately measured as a function of temperature [7]. Ordinarily, TMA involves measuring sample thickness changes with temperature, using a quartz probe maintained under a constant, low load. The atmosphere inside the chamber housing the sample is dry, inert gas, such as nitrogen. The mathematical quantity derived from TMA measurements obtained under these conditions, relating the variation in sample thickness with temperature, is referred to as the linear coefficient of thermal expansion (LCTE) [7].

A Mettler TMA 40 was used in this study. To determine the dimensional response of parchment with changes in RH, it was necessary to modify the instrument and the standard measuring procedure. Humidified air was used as purge gas by circulating the air over a saturated salt solution into the chamber by means of a small, piston-driven pump. Air, introduced through a metal tube passing through a rubber stopper at the top of the chamber, exited back to the salt solution (Figure 1). The RH within the sample chamber was monitored by means of a Shinyei hygromograph sensor.

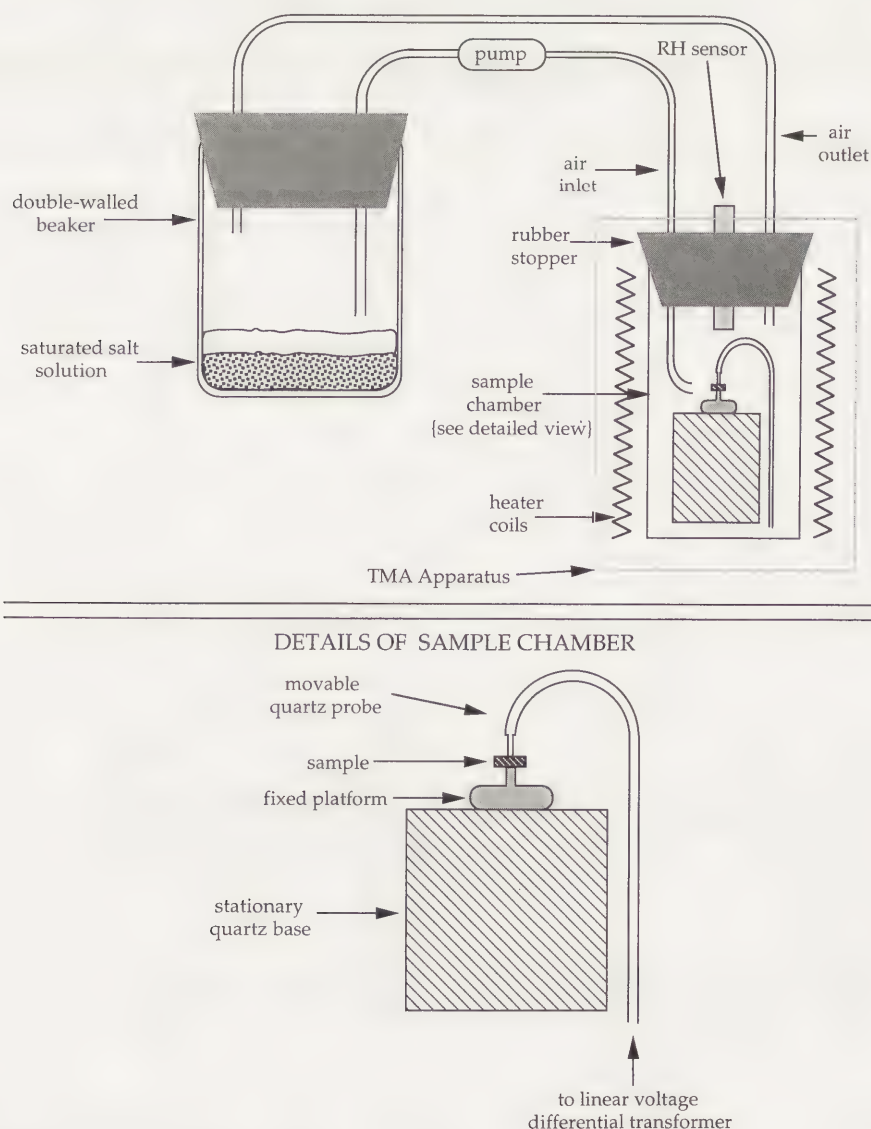


Figure 1: Diagram of modified TMA apparatus.

A constant temperature maintained inside the chamber eliminated thermal expansion effects of the scroll samples, and minimized RH fluctuations with temperature. Temperature variations were less than one degree over the course of a seven day experiment.

Using the aforementioned technique, the RH inside the sample chamber could be varied in a stepwise manner by exchanging saturated salt solution reservoirs. The RH within the sample chamber did not exactly match the RH directly over the salt solution because the chamber could not be perfectly sealed. As indicated by the humidity sensor, six minutes were required until the RH in the sample chamber changed from 70% to 30%.

In preliminary tests of ancient parchment fragments, irregularities were observed in the measurement data for RH steps below 30%. Presumably, the fragments were buckling or cupping due to differing hygric response between the hair side of the parchment and the flesh side. To minimize the influence of buckling on the experimental data, a small, 1 mm diameter quartz probe was used in place of the standard 3 mm probe. Additionally, a small metal platform with a flat 1 mm tip was placed on the quartz platform to support the samples. This system minimized the contact area between sample, the probe and the support. The probe force applied to the samples was 0.01N.

### Test Procedure

Small samples approximately 3 mm on a side were positioned on the platform with the concave side facing up, and the initial thickness recorded. After positioning the chamber, the reservoir containing saturated sodium chloride solution was attached to the pump, and the sample was allowed to equilibrate overnight at the initial RH level (approximately 70% RH).

Following overnight equilibration, the measurement program was initiated. After a five minute period during which the starting sample thickness was established, a reservoir containing saturated  $\text{Mg}(\text{NO}_3)_2$  solution was attached to the pump, and measurement continued until the equilibrium thickness was achieved at the new RH. Usually, this required from three to six hours, depending on the rate of dimensional change. In those instances in which an equilibrium thickness was not achieved after three hours (particularly for gelatin and ancient parchments), an exponential curve fitting analysis was performed in order to estimate the final equilibrium thickness. The best fit was found for the data beginning after 15 minutes, since approximately six minutes was required for the RH to attain the final value in the sample chamber.

The procedure thus described constitutes one analytical run. To obtain the dimensional response of a sample over a wide RH range, successive runs were carried out in which the RH was varied in a stepwise manner using different saturated salt solutions:  $\text{NaCl}$ ,  $\text{Mg}(\text{NO}_3)_2$ ,  $\text{K}_2\text{CO}_3$ ,  $\text{MgCl}_2$ ,  $\text{CH}_3\text{COOK}$ ,  $\text{LiCl}$ .

Five fragments of the Dead Sea Scrolls were measured in this study: Isaiah-B, Thanksgiving, Genesis Apocryphon, Temple-A and an unidentified Cave IV specimen. These samples were furnished for this study by Dodo Shenhav, Israel Museum. Initial samples thicknesses ranged from 300  $\mu\text{m}$  to 500  $\mu\text{m}$ . The Temple-A scroll fragment, which appeared to be consolidated with poly (vinyl acetate), exhibited severe buckling. An effort was made to remove the polymer prior to analysis, however, the results were similar. Therefore, no evaluation was performed on the data from the Temple-A scroll.

For comparative purposes selected reference materials were also measured: modern sheepskin parchment (obtained from Benjamin Vorst), modern gelatin (obtained from Kremer Pigmente, biological source unknown), and degraded modern parchment, made by exposing a sample of modern parchment to steam for 24 hours to convert collagen to gelatin. Examination of the degraded sample at 50 $\times$  magnification revealed areas of gelatin excretions, and an increase in overall sample thickness from 200  $\mu\text{m}$  to over 700  $\mu\text{m}$ .

It was found that scroll fragments tended to creep under constant load over long periods of time (2 to 10 days), especially above 45% RH. Thus, to minimize effects of creep, a standard time period of three hours was employed for the



analytical runs in this study. Table I lists the RH step data, as measured inside the TMA-40 sample chamber, for the entire set of samples examined in this study.

Table I. Percent relative humidity step data for selected materials.

Material tested	a	b	c	d	e	f	g	h
Modern parchment	69-47	47-38	38-30	30-70	70-30	30-28	28-16	16-70
Degraded modern parchment	68-47	47-37	37-28	28-68	68-30	30-23	23-16	16-70
Modern gelatin	68-46	46-38	38-30	31-70	70-30	30-27	27-16	16-68
Cave IV scroll	74-48	48-38	38-30	30-70	70-30	30-22	22-16	16-70
Isaiah-B scroll	70-45	46-38	38-32	32-70	70-29	28-22	22-16	16-70
Genesis apocryphon scroll	72-46	48-37	37-30	30-70	70-30	30-22	22-16	16-70
Thanksgiving scroll	72-46	46-38	38-30	30-68	68-32	32-22	22-16	16-74

### Results and Discussion

The results showed that differences exist in both the extent of dimensional change, and the overall rate of equilibration, for a given RH step jump. This is illustrated in Figure 2, an overlay of selected regions of the measurement curves for modern parchment, degraded modern parchment, modern gelatin and a sample of the Isaiah-B scroll. The scroll fragment responded more slowly to RH step changes, with smaller overall dimensional changes, than gelatin or modern parchment.

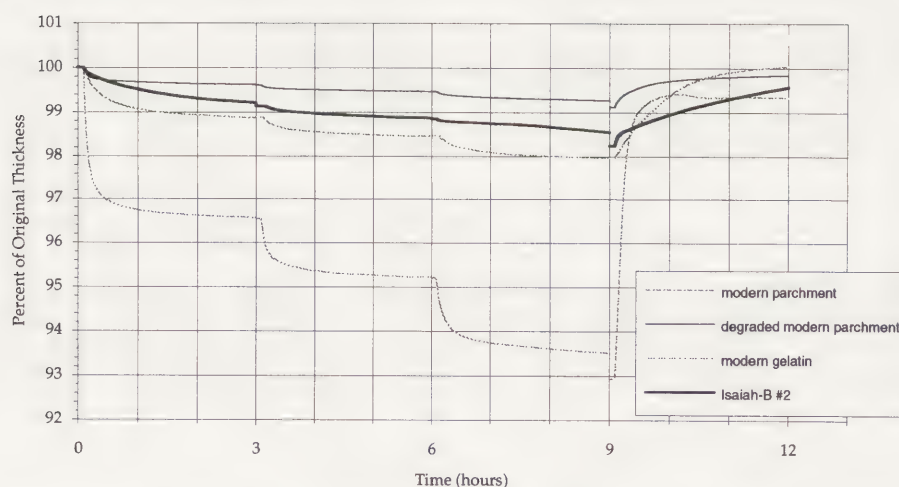


Figure 2: Comparison of dimensional response curves for selected materials: 0 to 3 hrs = 70 to 46% RH; 3 to 6 hrs = 46 to 38% RH; 6 to 9 hrs = 38 to 30% RH; 9 to 12 hrs = 30 to 70% RH.

Considering the nature of the TMA-RH step jump measurement results, several important parameters can be derived. The first is the relative amount of dimensional change for a given change in RH. This term, the percent RH analogy to the LCTE, was termed the "hygric expansion coefficient, or "HEC":

$$\text{HEC} = (\Delta \text{Thickness}) / \{(\Delta \% \text{ RH}) * (\text{initial sample thickness})\},$$

in units of  $(\% \text{ RH})^{-1}$ . (1)

Table II lists hygric expansion coefficients for each material tested, grouped by nominal RH step. HEC values fell in the  $10^{-4}$  range for most materials. The largest values were recorded for modern parchment (from  $14 \times 10^{-4}$  to  $35 \times 10^{-4}$ ) and the smallest for degraded modern parchment (from  $1 \times 10^{-4}$  to  $6 \times 10^{-4}$ ). The scroll fragments most closely resemble degraded modern parchment in their response, with values ranging from  $1 \times 10^{-4}$  to  $8 \times 10^{-4}$ . For a given material, the HEC values increased as RH fell below 30%, suggesting that 30% may be a critical RH level for collagen and gelatin.

Table II. Hygric expansion coefficients for selected materials\*.

Material tested	70-46	46-38	38-30	30-70	70-30	30-26	26-16	16-70
Modern parchment	16	14	29 <sup>a</sup>	16	16	18	33 <sup>a</sup>	19
Degraded modern parchment	2	1	4 <sup>a</sup> , 3 <sup>b</sup>	2 <sup>a</sup> , 2 <sup>b</sup>	2	6 <sup>a</sup>	5 <sup>c</sup>	3 <sup>c</sup>
Modern gelatin	5	5	9 <sup>a</sup>	6	5	10	15 <sup>a</sup>	7
Cave IV scroll	3	2	3 <sup>a</sup>	2	2	2	5 <sup>a</sup>	2
Isaiah-B scroll	4 <sup>b</sup>	4 <sup>b</sup>	10 <sup>a</sup>	5 <sup>b</sup>	4 <sup>a</sup> , 4 <sup>b</sup>	1	3	4 <sup>a</sup> , 4 <sup>b</sup>
Genesis apocryphon scroll	4 <sup>c</sup>	1	5 <sup>a</sup>	4 <sup>d</sup>	4 <sup>d</sup>	1	6 <sup>a</sup>	4 <sup>a</sup>
Thanksgiving scroll	5	2	2	3	—	1	2	3

Legend: Data based on final sample thickness obtained by: (<sup>a</sup>) overnight equilibration; (<sup>b</sup>) exponential curve fitting analysis; (<sup>c</sup>) six hour equilibration; (<sup>d</sup>) estimate of 100% due to irregularly-shaped curve and insufficient equilibration time.

\* HEC data listed times 10<sup>4</sup>/ % RH. HEC values are based on final sample thickness after three hours of measurement, unless otherwise noted. Two values may be listed under a particular heading to compare the results of curve fitting with the actual measured data. Column headings refer to nominal % RH steps. Actual % RH step data are listed in Table I, columns a-h.

The second important parameter to be considered is the rate at which the scroll fragments responded to changes in relative humidity. Given the variation in sample geometry, porosity and state of preservation of the scroll fragments, it was impossible to derive a full kinetic treatment of the measurement data without making unwarranted assumptions about the nature of the dehydration and re-hydration reactions.

Nevertheless, the half-time of reaction (water vapor exchange) served as an approximate measure of the rate of dimensional response. Half times for the set of data appear in Table III. Overall, modern parchment responded rapidly to changes in RH, with half times from 4 to 14 minutes, whereas gelatin and degraded modern parchment responded much more slowly (half times from 5 to 125 minutes). Table IV shows that Genesis Apocryphon, Thanksgiving, and Isaiah-B all resemble degraded modern parchment (half times ranging from 7 to 180 minutes), whereas the kinetic response of Cave IV (half times from 2 to 45 minutes) correlates with modern parchment.

Table III. Half times for selected materials\*.

Material tested	70-46	46-38	38-30	30-70	70-30	30-26	26-16	16-70
Modern parchment	4	5	14 <sup>a</sup>	5	4	5	13 <sup>a</sup>	6
Degraded modern parchment	5	10	115 <sup>a</sup>	17 <sup>a</sup>	9	180 <sup>a</sup>	45 <sup>c</sup>	27 <sup>c</sup>
Modern gelatin	15	20	47 <sup>a</sup>	39	19	17	125 <sup>a</sup>	45
Cave IV scroll	2	2	45 <sup>a</sup>	3	2	2	20 <sup>a</sup>	1
Isaiah-B scroll	45	55	180 <sup>a</sup>	90 <sup>b</sup>	70 <sup>a</sup>	90	85	80 <sup>a</sup>
Genesis apocryphon scroll	67 <sup>c</sup>	27	180 <sup>a</sup>	170 <sup>d</sup>	50	7	180 <sup>a</sup>	50
Thanksgiving scroll	21	6	6	—	—	—	6	—

Legend: Data based on final sample thickness obtained by: (<sup>a</sup>) overnight equilibration; (<sup>b</sup>) exponential curve fitting analysis; (<sup>c</sup>) six hour equilibration; (<sup>d</sup>) estimate of 100% due to irregularly-shaped curve and insufficient equilibration time.

\* Data given in minutes. Column headings refer to nominal % RH steps. Actual % RH step data are listed in Table I, columns a-h. When no half time value is given, the curve shape was too irregular for proper evaluation.

The observed differences in rates of approach to equilibrium among the various materials may be due to differences in the mode of water vapor transport through the pores in the open, fibrous structure of modern parchment versus gelatin-impregnated parchment. In the latter case, slower water vapor diffusion through the denser medium would lead to longer equilibration half-times. The Cave IV sample is anomalous in that the hygric expansion coefficient is low, indicating similarity to degraded parchment and gelatin, and yet the equilibration half-time is short, indicating similarity to modern parchment.



For individual samples, comparison of the half times for the RH step from 30% to 70% (rehydration) to the step from 70% to 30% (dehydration) also yielded interesting results. Dehydration and rehydration occurred at approximately the same rate for modern parchment and the Cave IV scroll. In contrast, rehydration occurred more slowly for gelatin, degraded modern parchment, and the scrolls Genesis Apocryphon, Thanksgiving, and Isaiah-B.

A tempting conclusion might be that the Cave IV scroll has suffered less physical deterioration than the other scrolls tested. Although the history and location where the tested Cave IV sample was discovered have not been documented, many of the Cave IV fragments were found buried in the floor of the cave and one can speculate that some degree of environmental protection was offered by the clay floor that enabled this fragment to retain an open structure that would permit rapid equilibration.

Another parameter which can be obtained from this study is whether or not scroll fragments undergo permanent deformation upon cycling to very low levels of relative humidity. Permanent deformation has been observed in earlier studies of the Dead Sea Scrolls using X-ray diffraction analysis. In this study, permanent sample deformation was indicated if the sample did not return to its original thickness (measured to within the reproducibility limit of  $\pm 0.1\%$ ) after the RH was restored to its original value at the beginning of the experiment (usually 70%).

Modern parchment underwent the largest degree of permanent deformation, losing approximately 0.75% of its original thickness after cycling to 30% RH, and approximately 1% after cycling to 16% RH. Modern gelatin returned to its starting thickness after cycling down to 16% RH. Degraded modern parchment and the scroll fragments exhibited a deformation of approximately 0.2% after cycling to 16% RH. This level of apparent deformation may be insignificant, due to the effects of creep.

The final observation which can be made from examination of the data concerns the shape of the dimensional response curves. In general, the dimensional response to changes in % RH tended to be exponential after the sample chamber attained the final value of RH. Non-exponential behavior began at levels of RH below 38% for the scroll fragments and for modern parchment. This information may relate to the results from dynamic mechanical analysis, which showed that near 30%, internal stresses within modern parchment became unreasonably large. However, more study is required to understand the relationship between stress and dimensional response.

## Conclusions

The results of this study revealed that RH-step jump thermomechanical analysis can provide useful information on the dimensional response of modern and ancient parchment to changes in relative humidity. Fragments from selected Dead Sea Scrolls were found to respond more slowly to RH fluctuations, and undergo smaller dimensional changes, than modern parchment under the same conditions. The hygric expansion coefficient data indicate that parchment fragments from the Genesis Apocryphon, Isaiah-B and the Thanksgiving scrolls behave more like degraded modern parchment and gelatin than undegraded modern parchment. The magnitude of the dimensional change that occurs on reducing the storage relative humidity is considerably smaller for degraded parchment than for modern parchment. Although the half-time for establishment of water vapor equilibrium is longer for degraded parchment than for modern parchment, the absolute response time is relatively rapid and care should be taken not to subject aged, brittle parchment to rapid dehumidification, particularly if the parchment is restrained.

Under the test conditions scroll samples, degraded modern parchment and gelatin showed little ( $<0.2\%$ ) permanent dimensional changes following RH cycling to 16%. This is in contrast to the 1% deformation shown by modern parchment. However, at low RH, brittleness and cockling become important

factors and a reasonable compromise RH between hygric expansion stability and mechanical stability seems to be  $35 < RH < 40\%$ .

### Acknowledgments

The authors wish to express their appreciation to Dodo Shenhav (Israel Museum) and Magen Broshi (Shrine of the Book) for providing the Dead Sea Scroll fragments used in this study, and to Frank Preusser (GCI) for his interest and encouragement.

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## Abstract

Recent advances in the design of infrared camera systems offers the opportunity to expand the usefulness and power of the technique of infrared reflectography (IRR). Specifically, platinum silicide (PtSi) cameras are now available as large format focal plane arrays. For this reason, we have undertaken the evaluation of platinum silicide cameras as tools for IRR. We present here a comparison of images acquired with infrared film, vidicon camera system and the PtSi camera system. It is apparent that the PtSi cameras offer both dramatically improved imaging performance and increased penetration of difficult pigments due to the combination of a solid-state detector with wide spectral response. The result is enhanced visualization of underdrawings and compositional changes.

## Keywords

Documentation methods, infrared reflectography, digital imaging

## Evaluation of Platinum Silicide Cameras for Use in Infrared Reflectography

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## Introduction

Infrared reflectography (IRR) has proven to be a valuable tool for the examination of paintings. Since the introduction of the vidicon camera in the late 1960s (1), the technique has found wide application throughout the museum community. Infrared reflectography has found particular use in the examination of Northern European paintings from the 15–16th centuries and has provided much information relevant to the interpretation of artist's techniques and workshop practices. Until recently, there has not been a critical evaluation of the performance of the vidicon camera in relation to the physical behavior of artist's materials in the near-infrared spectrum. Consequently, conservators have not appreciated the limitations of the vidicon camera system for this application and have not sought out improved imaging devices. A series of experiments suggested to us that improved detection of underdrawings would be possible using a solid-state detector system with a wide spectral response (2). Given the results of our analysis, we initiated an evaluation of platinum silicide (PtSi) cameras as tools for infrared reflectography. PtSi cameras offer the advantages of solid state detection systems, that is, low distortion, even responsivity, and high dynamic range. In addition, PtSi cameras are commercially available as large focal plane arrays that operate with video-speed readouts. Finally, PtSi cameras are sensitive in the 1.1–5.0 micron ( $\mu\text{m}$ ) region of the spectrum. We have completed the examination of a number of paintings with two of these cameras and present here a comparison of images acquired with infrared film, as well as images obtained using a vidicon and two PtSi cameras operating in different spectral bands. It is apparent that PtSi cameras offer a dramatic improvement in imaging performance and will expand the ease, usefulness, and power of the technique of infrared reflectography.

## Methods

Five camera systems were used to capture the infrared images discussed in the Results section (see the figures and the following section).

The reflected infrared photograph of the painting *Madonna & Child* by Domenico Veneziano appears to have been shot in the 1940s using Kodak high speed infrared 4143 film. It was printed as a standard developed-out gelatine print.

The vidicon reflectograms of the painting were imaged with a Hamamatsu C/2741-03 camera equipped with a N2606-10 lead sulfide tube, and a Nikon 55 mm macro f/2.8 lens fitted with a Wratten 87A filter. The resulting images were photographed from a Tektronix 634 monitor using Kodak T-Max 400 film and mosaiced with the conventional splicing method. The final composite was photographed with Kodak Professional Copy 4125 film and printed on Kodak Polycontrast III RC paper.

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The vidicon reflectograms of *The Crucifixion* by the workshop of Hans Mielich were imaged with a Hamamatsu C/1000-03 camera equipped with a N2606-10 lead sulfide tube, a Wratten 87A filter, and the Nikon lens used above.

For both paintings, the images in the 1.5–2.0 ( $\mu\text{m}$ ) spectral band were collected with the Eastman Kodak KIR-0330 PtSi Infrared Camera System. This camera system uses a Schottky-barrier focal plane array with  $640 \times 486$  detector elements and is cooled with liquid nitrogen. The camera was fitted with a combination of two filters: a 1.5  $\mu\text{m}$  cut-on filter (Corion # RL-1500-F) and a 1.2–2.0 band pass filter (Oriel # 57980). The Nikon lens used for the vidicon images was also used with the Kodak camera.

The images in the 2.2–5.0  $\mu\text{m}$  spectral band were collected with Mitsubishi Electric Corporation's PtSi Thermal Imaging Camera which uses a Schottky-barrier IRCSD focal plane array with  $512 \times 512$  detector elements and is cooled with a Stirling-Cycle cooler. The camera was configured to approximately the 2.2–5.0  $\mu\text{m}$  spectral region by fitting it with a germanium window and a Mitsubishi IR-L50C semi-germanium 50 mm f/1.2 lens.

The Hamamatsu C/1000-03 vidicon camera and the Kodak and Mitsubishi PtSi cameras were interfaced with a Macintosh Quadra computer *via* a Perceptics Pixelbuffer frame-grabber card. The digitized images were collected by averaging 8 frames using Signal Analytic's IP-Lab Spectrum. They were composited using Image (written by Wayne Rasband of the National Institutes of Health) and Adobe Photoshop, and were then output with a Kodak XL7700 continuous-tone dye-sublimation printer on Kodak Ektatherm print paper.

## Results

Domenico Veneziano's *Madonna and Child* (See fig. 1) was photographed in the 1940's with infrared film (fig. 2). Although the underdrawing painted with red



Figure 1: Domenico Veneziano, *Madonna & Child*, (Samuel H. Kress Collection).

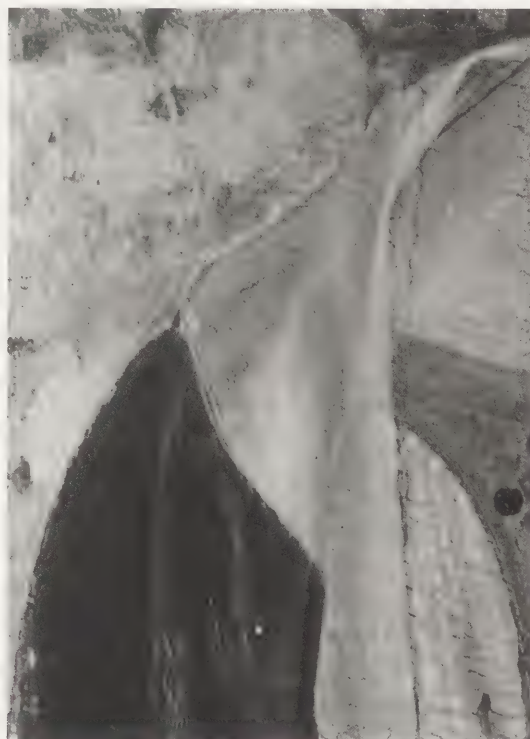


Figure 2: Detail of infrared photograph, 0.7–0.9  $\mu\text{m}$  spectral band.

lake in the Madonna's pink sleeve is clear and sharp, the drawing beneath the yellow lining of her cloak, painted with lead tin yellow and earth colors, is somewhat fainter. The blue cloak painted with azurite illustrates the great disadvantage of imaging in the region 0.7–0.9  $\mu\text{m}$ ; azurite absorbs in this spectral band and therefore masks the presence of the underdrawing.





Figure 3: Detail of infrared reflectogram, 0.9–1.4  $\mu\text{m}$  (composite: Barabara Pralle).

The vidicon, most sensitive in the 0.9–1.4  $\mu\text{m}$  region, partially penetrates the azurite, revealing faint indications of underdrawing lines in the shoulder (fig. 3).

In the areas where underdrawing is visible, the film image is easier to read than the vidicon composite because of the characteristically narrow dynamic range and lack of clarity. These problems are characteristic of vidicon images, which generally register only a narrow range of greys and have a low modulation transfer function (MTF) (3). Formally, the MTF is a plot of the expected visibility of an ideal set of parallel black lines as a function of the spacing between these lines. An ideal system would have a visibility of 1.0 for all resolvable spacing.

The same area imaged with a PtSi infrared camera system configured for the 1.5–2.0  $\mu\text{m}$  region offers dramatic improvements in penetration and resolution (fig. 4). The azurite robe is transparent in this spectral band. The extremely high dynamic range of the PtSi detector makes it possible to distinguish many more grey levels than the vidicon. With this image, it is possible to clearly distinguish at least two separate stages of underdrawings. A “paler” line is characterized by sketchy parallel marks which are found throughout the image, but are prominent at interior folds; they seem to constitute the first, roughly-drawn sketch of the composition and include changes made in the drapery folds. There is a second, “darker” line which appears to have been applied with a brush. This is a wider and bolder line which describes the outer contours of forms and defines the final composition.



Figure 4: Detail of infrared reflectogram, 1.5–2.0  $\mu\text{m}$  (composite: Elizabeth Walmsley).



Figure 6: Workshop of Hans Mielich, *The Crucifixion* (Samuel H. Kress Collection).



Figure 5: Detail of infrared reflectogram, 2.2–5.0  $\mu\text{m}$  (composite: Elizabeth Walmsley).

Finally, by configuring a PtSi camera system to work in the 2.2–5.0  $\mu\text{m}$  region, we acquired an image of completely different characteristics (fig. 5). This image is less contrasty overall and has a mottled appearance. In addition, the lead tin yellow highlights on the cloak are more conspicuous than in the previous images. The artifacts which register in this image are not completely understood at this time, and will be the subject of further study.





Figure 7: Detail of infrared reflectogram, 0.9–1.4  $\mu\text{m}$  (composite: Melissa Boring).



Figure 8: Detail of infrared reflectogram, 1.5–2.0  $\mu\text{m}$  (composite: Elizabeth Walmsley, Catherine Metzger and Stuart Wolffe).

Comparison of three infrared reflectograms of *The Crucifixion* attributed to the Hans Mielich workshop (fig. 6) acquired by the vidicon (fig. 7), the Kodak PtSi camera (fig. 8), and the Mitsubishi PtSi camera (fig. 9) further illustrates the differences in images obtained from the different spectral bands, as well as the improvement afforded by a greater dynamic range and resolution.

The vidicon image exposes a pattern of grid lines laid onto the panel as an aid to transfer the design, and close study reveals some freely-sketched brush underdrawing and a row of male heads (now overpainted) along the bottom edge of the panel. The 1.5–2.0  $\mu\text{m}$  image renders both grid lines and underdrawing (see the circular form at the bottom left of the image) more legible. The heads are visible in the vidicon mosaic but because the image is exceedingly flat, there is little definition of different regions of the faces. The 2.2–5.0  $\mu\text{m}$  image again presents a different aspect of the painting. As noted with the Domenico Veneziano images, many of the underdrawing lines are distinguished from the background only with difficulty, while some of the changes in paint layers are more legible. Here, the grid lines have all but disappeared, yet two red crosses, now partially overpainted, are prominent.



Figure 9: Detail of infrared reflectogram, 2.2–5.0  $\mu\text{m}$  spectral band (composite: Elizabeth Walmsley and Colin Fletcher).

### Conclusions

The improved imaging performance of PtSi cameras can be determined from the operating specifications of the array and camera system, as well as the physical characteristics of the solid-state detector material. We used two equivalent PtSi cameras to produce the images presented here. Because these cameras are sensitive in a wide region of the infrared, they were configured to work in two different spectral bands. We found subtle but potentially important distinctions between the resulting images. It appears that the 1.5–2.0  $\mu\text{m}$  region is optimal for imaging underdrawing materials such as chalk, charcoal, metals, and inks (4). However, as demonstrated here, the 2.2 to 5.0  $\mu\text{m}$  band reveals compelling but uncharacterized reflectograms which suggest that compositional changes, specific pigments, and/or surface features are being imaged. Interestingly, this configuration allows infrared cameras to detect signals in a spectral region where the painting is emitting heat. It is possible that some differences in the relative heat emission or reflection may be contributing to the features that are imaged. The use of PtSi cameras to determine the optimal spectral band for particular underdrawing/paint combinations will be the subject of continuing study.

### Acknowledgements

We acknowledge support from the Circle of the National Gallery of Art. We also acknowledge Raymond Rehberg of Eastman Kodak (Electro-Optics Division) for the reconfiguration and loan of the Kodak PtSi Infrared Camera System, Michael Mays of Mitsubishi Electronics America, Inc. (Thermal Imaging Products) for the loan of the Mitsubishi PtSi Thermal Imager IR-M500, Edwin Sutter of Sutter & Company for the loan of the Hamamatsu C2741 vidicon camera, and Barbara Berrie of The National Gallery of Art, Washington, DC (Scientific Research Department) for the microscopic analysis of the Domenico Veneziano.

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# Subgroup

Study of Painting Techniques

Etude des techniques de peinture





## Résumé

Présentation d'un projet d'étude de la technique picturale de Pieter Bruegel l'Ancien, fondé sur des radiographies, photographies et réflectogrammes en infrarouge, réalisés par l'Institut royal du Patrimoine artistique (Bruxelles). Exposé des résultats obtenus à ce jour pour deux oeuvres majeures: la *Chute des anges rebelles* et le *Dénombrement de Bethléem*. Leur technique est caractérisée par une extrême économie de moyens, alliée à une parfaite aisance d'exécution. L'élaboration picturale se réduit à un travail de surface sur une couche de fond blanche; la richesse expressive résulte de la multiplicité des effets de facture et d'écriture. Si l'on en juge d'après les documents disponibles à l'heure actuelle, le dessin sous-jacent consiste en une esquisse de composition, sans indications de modelé ou de clair-obscur.

## Mots-Clés

Bruegel, dessin sous-jacent, technique picturale

## Approche de la technique picturale de Pieter Bruegel l'Ancien

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### Présentation de la démarche

Parmi les artistes flamands du XVI<sup>e</sup> siècle, Bruegel se signale non seulement par une inspiration débordante, mais aussi par un métier admirable. Sa technique picturale est en harmonie avec son style: étourdissante de simplicité, de spontanéité, d'aisance, en un mot: magistrale. Lors d'une exposition intitulée "Bruegel, le peintre et son monde", tenue aux Musées royaux des Beaux-Arts de Bruxelles en 1969, ses caractéristiques majeures furent mises en lumière, documents à l'appui. Les auteurs de cette démarche, Albert Philippot, Jacqueline Folie et Régine Guislain-Wittermann, en présentèrent les résultats aux visiteurs sous la forme de panneaux didactiques. Ils offraient là une synthèse extrêmement éclairante: on regrette qu'elle n'ait jamais été publiée. En 1979, Catheline Périer-d'Ieteren émit quelques observations pénétrantes sur la technique du maître, dans un article où elle retraçait l'évolution de la technique picturale flamande du XV<sup>e</sup> au XVII<sup>e</sup> siècle. Elle soulignait combien le rôle de Bruegel avait été décisif dans cette évolution (1).

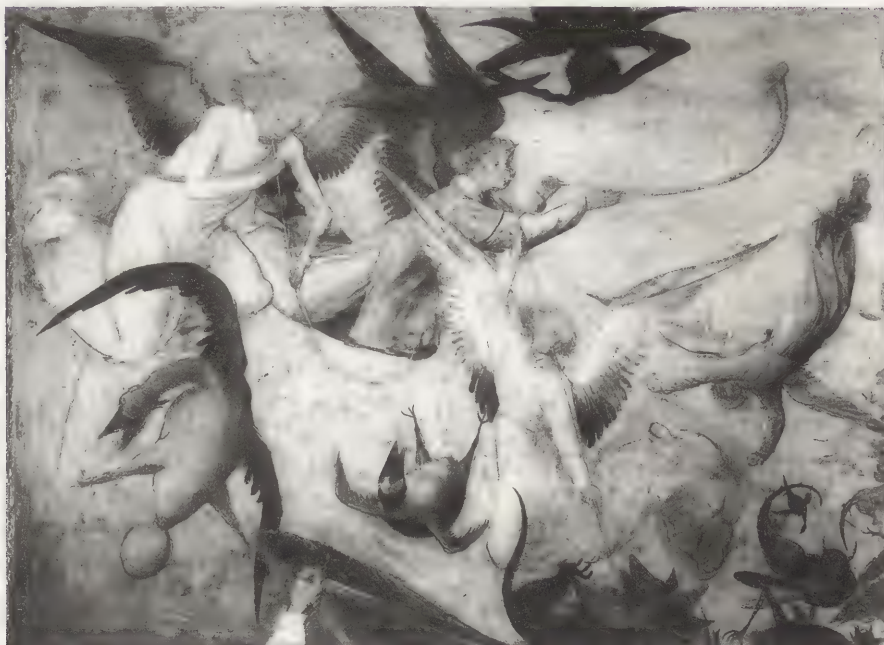
Il y avait certes là matière à éveiller l'intérêt des milieux scientifiques. Et pourtant, aucune recherche ne fit suite à ces préalables prometteurs. C'est tout récemment qu'un projet a vu le jour, à l'initiative conjointe de l'Institut royal du Patrimoine artistique de Bruxelles (IRPA) et du Service d'histoire de l'art des temps modernes de l'Université de Liège. Il consiste, dans un premier temps, à étudier les tableaux conservés dans les collections publiques belges. Pour nombre d'entre eux, des dossiers existent déjà à l'IRPA; ils ont été constitués à l'occasion de traitements de conservation ou de restauration. C'est le cas pour deux chefs-d'oeuvre du peintre, conservés aux Musées royaux des Beaux-Arts de Bruxelles: la *Chute des anges rebelles* (signée et datée 1562) (2) et le *Dénombrement de Bethléem* (signé et daté 1565) (3). Ceux-ci ont été choisis comme supports des premières analyses. Deux tableaux plutôt qu'un seul, car s'il est légitime de caractériser la manière propre de Bruegel, il importe aussi d'en saisir les nuances, les inflexions, suivant les effets que celui-ci cherchait à suggérer. Or ces effets diffèrent radicalement dans les deux peintures en question: d'un côté, une composition tout en mouvements, avec de forts contrastes d'ombre et de lumière, de l'autre, une composition statique, baignée d'une atmosphère pâle.

### Le dessin sous-jacent

Peu de documents sont disponibles à ce jour, permettant l'étude du dessin sous-jacent chez Bruegel. L'IRPA possède quelques photographies à l'infra-rouge et quelques réflectogrammes. On peut en dégager certaines observations, étant entendu que celles-ci demanderont à être vérifiées par des investigations plus systématiques. Le dessin sous-jacent, dans les deux oeuvres envisagées, est effectué à la pierre noire. Il semble se limiter à une esquisse de composition.

Sur cette photographie à l'infrarouge du coin supérieur droit de la *Chute des anges rebelles*, par exemple (voir fig. 1), on constate que les formes sont campées par des traits vifs et fermes, mais allusifs: l'artiste ne s'est nullement soucié de les parachever. Il s'est contenté de dessiner les contours, ajoutant toutefois quelques détails expressifs: arêtes des plis d'un vêtement, traits d'un visage. L'esquisse ainsi composée n'accuse ni repentirs, ni reprises de forme significatives. Le tracé assuré révèle que Bruegel avait, dès le départ, une idée claire de sa composition. Sans doute travaillait-il d'après un modèle élaboré préalablement. Ce modèle devait aussi lui permettre de ménager les effets d'ombres et de lumières, lors de l'exécution picturale. Dans les deux oeuvres étudiées, en tout cas, le dessin sous-jacent paraît dépourvu d'indication de modelé; aucune hachure n'a été relevée. De ce point de vue, il est intéressant de confronter des réflectogrammes IR

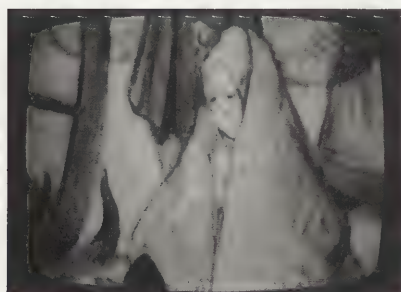




1. Pieter Bruegel l'Ancien, *La chute des anges rebelles*, 1562, Bruxelles, Musées royaux des Beaux-Arts. Photographie à l'infra-rouge du coin supérieur gauche. Copyright A.C.L.—Bruxelles.



2. Pieter Bruegel l'Ancien, *Le dénombrement de Bethléem*, 1566, Bruxelles, Musées royaux des Beaux-Arts. Réflectogramme: le buste de la Vierge. Copyright A.C.L.—Bruxelles.



3. Pieter Bruegel le Jeune, *Le dénombrement de Bethléem*, copie d'après Pieter Bruegel l'Ancien, Bruxelles, Musées royaux des Beaux-Arts de Bruxelles. Réflectogramme: le buste de la Vierge. Copyright A.C.L.—Bruxelles.

montrant un même détail, d'une part dans la version originale du *Dénombrement* (voir fig. 2), et d'autre part dans une de ses copies par Pieter Bruegel le Jeune (Musées royaux des Beaux-Arts de Bruxelles) (voir fig. 3). A la mise en place sommaire des contours principaux dans l'original s'oppose le dessin plus scrupuleux et plus détaillé dans la copie. Mais surtout, dans cette dernière, on découvre que les plans d'ombre sont localisés par des hachures.

### La structure de la couche picturale

La préparation faite de craie + colle est entièrement recouverte d'une mince couche de blanc de plomb, appliquée à coups de brosse larges et vigoureux, très perceptibles en radiographie. Cette couche de fond blanche ne remplit pas la même fonction dans les deux tableaux. Dans la *Chute des anges rebelles*, elle joue le rôle d'une *imprimatura* classique: elle rehausse l'éclat des couleurs, soit qu'elle transparaisse sous les glacis, soit qu'elle se laisse deviner, çà et là, entre les touches plus couvrantes. Dans le *Dénombrement*, elle conditionne de manière plus décisive l'effet final. En effet, dans cette composition largement dominée par le blanc, elle tient lieu de ton moyen. La matière picturale est appliquée par frottements tantôt légers, tantôt plus serrés: ainsi l'artiste suggère-t-il l'épaisseur cotonneuse de la neige; des glacis rendent les ombres, voilent le ciel d'un gris acier, suggèrent la translucidité de l'étang gelé; seuls les personnages, les arbres et les bâtiments sont traités en demi-pâte. Les formes les plus sommaires peuvent être réservées dans le blanc (les poules, au premier plan); les formes plus complexes s'y superposent (les branchages). A l'image de cette structure "minimaliste", le jeu des densités enregistré par la radiographie se fait extrêmement subtil (voir fig. 4). Ainsi, les toits enneigés de l'auberge à gauche, ou ceux de la grosse bâtisse au centre, ne se marquent guère. La couche de fond y est à peine retravaillée: seuls les contours sont repris d'un trait de pinceau fortement chargé de matière. C'est une particularité remarquable de ce tableau que cette formule qui consiste à ourler arêtes et contours d'un trait blanc épais. On relève aussi de vigoureux empâtements dans le rendu de quelques détails: les bâches et les roues des chariots, les boules de neige. Accentuant ainsi, en des points très précis, l'épaisseur de la matière picturale, l'artiste parvient à rendre sensibles les reliefs que forme la neige accumulée, et le scintillement de la lumière qui s'y accroche.

Dans la *Chute des anges rebelles*, on retrouve les mêmes rehauts épais sur les reliefs, par exemple dans la cote de maille du personnage casqué à droite. Ici, la radiographie révèle un registre de densités plus étendu, à l'image d'une palette plus contrastée (voir fig. 5). La composition y est très lisible. Point d'empâtements





4. Pieter Bruegel l'Ancien, *Le dénombrement de Bethléem*. Montage des radiographies de détail. Copyright A.C.L.—Bruxelles.



5. Pieter Bruegel l'Ancien, *La chute des anges rebelles*. Radiographie de détail: personnage à la tête casquée, à droite. Copyright A.C.L.—Bruxelles.

inutiles: seules les accents lumineux et les couleurs à forte teneur en blanc se marquent sur la pellicule; pour le reste, la couche picturale est à nouveau extrêmement fine. Voilà qui nous renforce dans notre conviction que l'artiste se référait à un travail préparatoire où les valeurs lumineuses, voire les couleurs, étaient déjà localisées.

### L'écriture picturale

On a vu que la structure picturale était élémentaire. A la savante superposition des couches qui faisait la qualité de la peinture des Primitifs flamands, s'oppose ici une manière nouvelle, simplifiée: chez Bruegel, tout le travail s'opère en surface. Une autre approche du métier s'impose alors. Les effets de facture revêtent désormais une importance capitale; c'est d'eux que va dépendre, pour une large part, la richesse expressive des oeuvres. D'une sensibilité et d'une sûreté inouïes, l'écriture de Bruegel lui ouvrait toutes les possibilités: c'est elle qui lui permettait de "rivaliser avec la nature", comme on disait à l'époque. Et l'on reste confondu devant l'éventail des effets obtenus. Un travail "léché" restitue les textures homogènes, comme la couche de neige intacte dans le *Dénombrement*; les coquilles, ou l'épiderme de certains animaux, dans la *Chute des anges rebelles*. Dans le *Dénombrement*, un "jus" brunâtre, hâtivement badigeonné sur la couche de fond blanche, donne consistance au crépis des murs de l'auberge, à gauche. Appliqué en touches parallèles, ce même "jus" rend tangible la texture des boiseries. Des glacis gris bleu, étendus en longs traits horizontaux, irrégulièrement fondus les uns dans les autres, parent la surface de l'étang gelé d'un éclat vitreux. Le même procédé est employé pour le ciel: les coups de pinceau forment une trame tantôt serrée, tantôt plus lâche, laissant entrevoir la couche de fond claire, suggérant une atmosphère incertaine, entre chien et loup. Le ciel est rendu de la même façon dans la *Chute des anges rebelles*, mais ici, les touches jaillissent à partir du disque de lumière pour s'éparpiller en tournoyant, contribuant au dynamisme de la composition. Dans les deux tableaux, chevelures, fourrures, plumages, sont obtenus par l'application de touches fines, de longueur variable, tantôt souples, tantôt drues, sur un ton de base uni.

Le modelé est travaillé dans le sens des formes, par des gradations lumineuses presque insensibles quand il s'agit de textures mates, plus vigoureuses quand il s'agit de surfaces brillantes (les casques et les armures dans la *Chute des anges rebelles*, par exemple). Dans les vêtements et les drapés, le pinceau suit les reliefs et les creux, souligne le tomber des étoffes, et accentue ainsi le dynamisme des figures. Ainsi, dans la *Chute des anges rebelles*, la radiographie a révélé, pour les

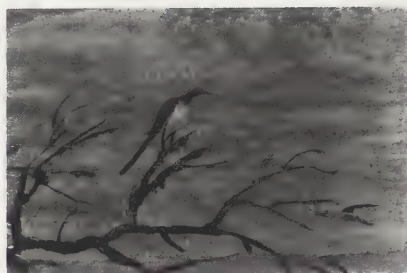


6. Pieter Bruegel l'Ancien, *La chute des anges rebelles*. Radiographie de détail: le vêtement de l'archange de droite. Copyright A.C.L.—Bruxelles.

figures d'archanges en plein mouvement, une peinture extraordinairement gestuelle, parfaitement accordée à la violence du sujet (voir fig. 6).

Détails et accidents de surface sont rendus par des rehauts graphiques. Dans le *Dénombrement*, les visages des paysans sont burinés par des petits traits aigus, accentuant leurs expressions jusqu'à les rendre caricaturales. Le procédé est omniprésent dans la *Chute des anges rebelles*: d'un pinceau fin mais fortement chargé de blanc, l'artiste redessine les reliefs, cerne les arêtes, les rides et les replis, marque les irrégularités. Il en résulte une image radiographique spectaculaire, où regards exorbités, mâchoires béantes, grimaces monstrueuses ressortent vivement. Le document offre ainsi la quintessence expressive de cette stupéfiante composition (voir fig. 5).

Si l'écriture de Bruegel révèle un virtuose de génie, c'est aussi parce qu'elle ne laisse deviner aucune hésitation, aucun effort. Fougueuse dans la *Chute des anges rebelles*, elle contribue à dynamiser la composition. Compte tenu de son ambiance plus sereine et de l'échelle réduite de ses figures, le *Dénombrement* réclamait un travail certes plus posé. La spontanéité du trait y est pourtant remarquable. Le fameux motif de la pie, perchée sur une branche du grand arbre, en offre un exemple éloquent : on y sent encore l'élan des trois coups de pinceau par lesquels l'artiste est parvenu à camper l'oiseau (voir fig. 7).



7. Pieter Bruegel l'Ancien, *Le dénombrement de Bethléem*. Détail en lumière normale: la pie perchée sur une branche du grand arbre à gauche. Copyright A.C.L.—Bruxelles.

### Conclusions et perspectives de recherches

Chez Bruegel, l'extrême simplification de la structure picturale s'opère au profit d'une diversification des effets de facture et d'écriture. Sur ceux-ci repose désormais une part importante du potentiel suggestif des oeuvres. On relèvera, comme caractéristiques distinctives, les empâtements vigoureux marquant les hautes lumières, et les rehauts graphiques accentuant lignes de force et détails expressifs. La nervosité du travail est également un trait à épinglez: Bruegel révolutionne la technique flamande traditionnelle en y introduisant l'exigence du "fare presto".

Le dessin sous-jacent corrobore l'impression d'une exécution rapide et sûre à la fois, suggérant que l'artiste s'appuyait sur des travaux préparatoires très fouillés. Son étude devra être approfondie: il y a beaucoup à attendre d'investigations systématiques en réflectographie à l'infrarouge. Une campagne d'examens selon ce procédé est prévue en 1993.

Des attributions litigieuses pourront être examinées à la lumière des résultats obtenus ici. Au vu des documents disponibles actuellement, les doutes émis quant



à l'authenticité de la *Chute d'Icare*, notamment, ne font que se confirmer. L'étude de cette oeuvre compte parmi les objectifs immédiats que s'est assignée l'équipe de travail.

### Remerciements

Pour le soutien qu'elles apportent au projet présenté ici, je tiens à exprimer ma gratitude à Madame L. Masschelein, directeur de l'IRPA, et à Madame E. de Wilde, conservateur en chef des Musées royaux des Beaux-Arts de Belgique. Mademoiselle J. Folie, chef de travaux à l'IRPA, m'a communiqué les documents réalisés lors de l'exposition de 1969. Je la remercie vivement pour l'aide qu'elle m'a apportée. Enfin, je sais gré à Madame Catheline Périer-D'Ieteren pour les conseils qu'elle m'a prodigués en vue de la rédaction du présent article.

### Notes

- (1) "L'application des méthodes physiques d'examen à l'étude du modelé dans la peinture", dans *Annales d'histoire de l'art et d'archéologie*, (Université libre de Bruxelles), 1979, pp. 41-56.
- (2) Panneau, 118,5 × 162,5 cm, inv. n° 584. Pour une approche stylistique, cf.: *Le siècle de Bruegel*, cat. expo., Bruxelles, Musées royaux des Beaux-Arts, 1963, n° 52; Fr. GROSSMANN, *Pieter Bruegel. Complete edition of the paintings*, 3e éd. Londres, 1973-1974, p. 192; R.-H. MARIJNISSEN, *Bruegel. Tout l'oeuvre peint et dessiné*, Anvers, 1988, p. 180-186 (avec indications bibliographiques complémentaires).
- (3) Panneau, 115,5 × 164,4 cm, inv. n° 3637. Pour une approche stylistique de cette oeuvre, cf. Catalogue de l'exposition de Bruxelles (*Op. cit.*: voir note 2), n° 53; Fr. GROSSMANN, *Op. cit.*, p. 199; R.-H. MARIJNISSEN, *Op. cit.*, p. 296-303.

## Abstract

Dosso Dossi was a court painter at the Este Court in Ferrara from c. 1514 to 1542. The Dukes of Este were grand patrons of the arts and commissioned works from the greatest living artists. A technical investigation of Dosso's oeuvre has been initiated in order to establish a chronology, if possible, and to better understand the influences of other artists on his methods and materials. Thus far, a small group of paintings, which were probably executed in the early 1520s, has been examined. The results suggest that Dosso was rather consistent in his working methods. These methods are similar to, but distinct from, those described in published work on Venetian artists and are comparable to Vasari's descriptions of painters' techniques.

## Keywords

Dosso Dossi, materials and methods of painting, analysis, pigments

## A Technical Investigation of the Materials and Methods of Dosso Dossi

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## Introduction

Dosso Dossi was a court painter in Ferrara from 1514 until his death in 1542. Until 1534, Alfonso I D'Este was Duke of Ferrara. He reigned over a court famed for, among other things, its artistic patronage and licentious behavior. Alfonso I commissioned works of art for his palaces and houses from the most famous artists of the time. Paintings by Rogier van der Weyden, Bellini, and Titian hung on the walls. Dosso was surely influenced by these artists' works. He may have been trained in Venice or Mantua, and he certainly travelled with Titian to Mantua in 1519 to see Mantegna's works. There has been some difficulty in establishing Dosso's stylistic development and it is difficult to establish his oeuvre only on stylistic grounds. We are conducting technical examinations of his paintings to determine whether there are any developmental trends in his painting technique which could assist in understanding the chronology of his work.

We have looked at several paintings by Dosso in order to ascertain his choice of materials and methods. At this point, we are presenting a summary of our discoveries thus far. Comparisons within the small group studied and to some Venetian works will be made. We will eventually make a careful comparison of Dosso's painting methods to those of his contemporaries.

## Results and Discussion

A small group of paintings by Dosso has been examined: *St. Lucretia*, c. 1520; *Circe and Her Lovers in a Landscape*, c. 1525 (See fig. 1); *The Battle of Orlando and Rodomonte*; *Scene from a Legend*, mid-1520s; and *Holy Family*, mid-1520s (1-5). Descriptions of the paintings are given by Gibbons (6). His general technique has been established by examination using the stereo microscope and x-radiog-



Figure 1. *Circe and Her Lovers in a Landscape*.

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Figure 2a. Cross section from *Scene from a Legend* taken from the green foreground at  $1.4 \times 5.9$  cm, showing the gesso ground, grey imprimatura, and green paint.



Figure 2b. The same cross section as in Figure 2a after staining for protein with AB3, showing the presence of a glue sealing between the gesso and the imprimatura.



Figure 2c. Cross section from *Circe* showing the gesso, grey imprimatura, and light blue sky paint. All sections photographed at  $\times 120$ .

raphy. Further details of execution and pigment identification have been determined using cross sections.

*St. Lucretia* and *Holy Family*, the smallest works of art in this study, are painted on wood. The other paintings are on fabric. Within Dosso's surviving oeuvre, the paintings are fairly equally distributed between wood and fabric supports.

All the paintings have a gesso ground. The cross sections from *Orlando and Rodomonte* do not contain the ground; however, from surface examination, the ground can be seen. The gesso ground, even on the paintings on fabric, is thick (over 100 microns). X-ray powder diffraction of the ground from *Circe* and from *Scene from a Legend* showed the presence of both gypsum and anhydrite. There is no evidence at this time that this reflects the use of *gesso grosso* and *gesso sottile*, though this is possible. Gettens and Mrose stated there is no outcrop of gypsum with anhydrite in Italy so the occurrence of the anhydrous calcium sulfate with gypsum suggests the use of a particular method of roasting the native material (7).

Staining with amido black showed that the ground has been sealed by a thin glue layer in *Circe* and *Scene from a Legend*, but there was no evidence of this in *St. Lucretia* or *Holy Family* (8). Gesso grounds were often, but not always, sealed with a glue layer. Examples have been noted in early Venetian and Ferrarese paintings (9, 10). Vasari described how an artist should "spread over [the gesso] with a sponge four or five coats of the smoothest size" (11). The practice of sealing gesso or plaster grounds before painting in oil was a well-established technique, mentioned by Cennini (12). Perhaps we are not always able to recognise the glue layer owing to its thinness.

All the paintings we have examined through cross sections have a grey-colored oleaginous imprimatura. In each painting, the imprimatura comprises lead white, charcoal, brown earths, and a high proportion of extenders. The color is darkest in *St. Lucretia*. A colored imprimatura was also noted by Braham and Dunkerton in a ceiling tondo painted by Dosso before 1525 (13). The grey imprimatura is, in fact, present in all the paintings by Dosso that have been examined thus far and can be seen in the cross sections in figure 2.

An imprimatura such as this has not been noted frequently. However, grey imprimaturas have been noted in some contemporary paintings by Titian (*Pala Pesaro*, 1519–1526), M. Basaiti (*San Giorgio e la Principessa*, 1520), and L. Lotto (*San Nicola in Gloria*, c. 1529) (14). Titian, Basaiti, and Lotto were not as consistent in their use of colored imprimaturas at this time as Dosso seems to have been. Furthermore, the general use of colored imprimaturas postdates Dosso's firm employment of the grey imprimatura. Vasari described the use of colored imprimaturas thus:

But first there must be made a composition of pigments that possess seccative qualities as white lead, dryers, and earth such as is used for bells, all thoroughly mixed together and of one tint, and when the size is dry this must be plastered over the panel and then beaten with the palm of the hand, so that it becomes evenly united and spread all over, and this many call the "imprimatura" (15).

The information obtained from cross sections of the paintings suggests that the mixture Dosso used was similar to this description. A full investigation of this layer using energy-dispersive spectrometry is planned in order to characterize the components more completely.

The x-radiographs indicate something of Dosso's method of paint application. There are underlayers that are laid down with a broad brush using an energetic swirling motion. The broad movements of the composition are delineated with the painted brushstrokes. No cross sections obtained to date have any evidence of a traditional underdrawing. The use of the grey imprimatura makes conventional infrared reflectography difficult to use for the visualization of any possible underdrawing. The x-radiography of *Circe* shows how Dosso laid out the general composition. The horizon and sky were painted over the imprimatura in broad, bold, fluid strokes, leaving the large trees in reserve.





Figure 3a. Detail of *Circe*.



Figure 3b. X-radiograph of the same area, showing major changes made when Dosso painted over a lion and covered it with landscape forms, including a dark brown bank. This x-radiograph also illustrates the broad brushwork in the landscape compared to the precise detail in the animals.

The x-radiographs of the paintings show many changes. Some are small while other suggest major changes in composition. For instance, even in the small panel of *St. Lucretia*, there are changes, including the direction in which the palm is leaning. In the painting of *Circe*, there have been a variety of significant and minor changes. On the level of details, Dosso's struggle with placement of Circe's hand is evident in the many fingers that can be seen on the tablet, the variation in the cant of her head, and the changes in the outline of the dog and its collar. On a grander scale, there is an enormous change in the whole composition in the obliterating of a lion and a deer; now, these figures are covered by landscape details: a path, green grass, and a dark brown bank that is covered with characteristic, cascading, snake-like roots. The changes in this painting are major and suggest that if a preliminary drawing was made, it was drastically altered during the process of painting. Figures 3a and 3b show details of the scale of change made by Dosso in *Circe*.

The x-radiography of the small panel of the Holy Family shows that it was painted over a portrait of a female. The x-radiograph has been published by Gibbons (16). The cross sections seem to suggest that, amazingly, Dosso did not paint out the first picture, which is entirely unrelated to the image of the Holy Family. Rather, he used fields of color from the first picture in the second. Such an adaptation, even if the new composition was one that Dosso was repeating and accustomed to, seems bold.

Cross sections show that Dosso, even when he was changing the pictorial composition, worked with a few layers of paint. The structure is often only a single layer of paint over the colored imprimatura. Leaves, clouds, and other details are added also in few layers over the sky. Indeed, one might say that Dosso created his pictures with a remarkable economy of effort.

Dosso has been noted not only for his enigmatic iconography, but also for his use of a high key palette. X-ray fluorescence spectroscopy and optical microscopy were performed to try to determine the palette of the paintings in the National Gallery collections (17). Only optical microscopy was used to examine the other paintings. In all instances, the palette appears to be fairly limited, comprising the following pigments: lead white, azurite, iron earths, lead-tin yellow, vermilion, red lake, and a copper green pigment. In *Scene from a Legend*, the orange paint is predominantly a mixture of lead-tin yellow and vermilion. By way of contrast, Bellini used orpiment and realgar to paint Silenus' orange drapery in *The Feast of the Gods* (18). Dosso used lead-tin yellow sparingly in many colors, e.g., the flesh tones, brown foliage, and brown tree trunks, but he did not necessarily use it in more yellow areas. For instance, the gilded edges of the pages of Circe's spell book contain no lead-tin yellow, only iron earths. In later studies, we will continue our examination of Dosso's palette to explore his possible use of orpiment and realgar, since comparison to the Venetian palette is interesting and there is evidence that Dosso travelled to Venice to obtain pigments.

X-ray powder diffraction analysis of the lead white pigment found in *Circe* shows it is not the typical pure basic lead carbonate, rather the pigment is a mixture of basic lead carbonate (hydrocerussite) and normal lead carbonate (cerussite). This mixture was previously noted in the white priming of *The Feast of the Gods*, although the paint in that picture contained only the hydrocerussite form of lead carbonate (19). The occurrence of cerussite and hydrocerussite together, especially with a large proportion of the former, is not frequently encountered. It may suggest a particular manufacturing process (20).

It has been observed that the green drapery in Dosso's paintings is often well-preserved. The cross section from Circe's drapery helps us realize why this may be so. While most sections from Dosso's paintings show very few layers of paint, the section from the drapery contains at least four layers of green paint. All are mixed from lead white and an uncharacterized copper green pigment. The layers are all a similar hue. Further work is being undertaken to identify the green pigment. The depth of green paint and the number of layers explain the distinct difference in appearance from, for instance, the green of the distant trees which has almost entirely disappeared. The multiple layering may also



suggest Dosso's reworking of the drapery. Unfortunately, a thin, irremovable scumble of a restorer's chrome green covers much of the original drapery. In none of the paintings has malachite or green verditer been found, although this pigment has been seen not only on contemporary Venetian pictures, but also on Cossa's *St. Vincent Ferrer* (21). The only blue pigment we have found in the paintings we have examined is azurite. Ultramarine was found by Braham and Dunkerton as an added layer to a finished, varnished painting and the bursar documented payment for the costly pigment (22). Paintings by Bellini and Titian for Alfonso I contain lavish amounts of ultramarine. The absence of this pigment in the paintings we have studied by Dosso, while not remarkable, might suggest they were not intended for important sites.

### Conclusions

The small group of paintings we examined that were executed by Dosso in the 1520s shares common painting methods. All the paintings, whether on panel or canvas, have a gesso ground. In two cases, this was shown to be a mixture of gypsum and anhydrite in glue. In many cases, a thin layer of glue isolating the gesso from the overlying oleaginous layers can be discerned following staining using Amido Black 3. In every instance, a grey-brown imprimatura lies below the paint films and on the gesso or glue isolating layer. The tone of the imprimatura varies, but the composition is always similar, i.e., lead white, earth pigments, extenders, and charcoal. In general, the paint is laid down in a direct and straightforward manner. An exception appears to be green drapery, which is sometimes created using multiple layers. Dosso's palette is fairly simple, containing the following pigments: lead white, iron earths, lead-tin yellow, vermilion, azurite, red lake, black, and copper green. Ultramarine is rarely encountered. The use of orpiment and malachite or green verditer is not confirmed, but will be investigated. In general, Dosso used methods that are well-matched to those Vasari described decades later. The concordance of details, as well as the similarity of techniques to those used by Dosso's contemporaries, will be investigated in the future.

### Acknowledgements

We should like to thank Jennifer Spohn and Michael Duffy of the Worcester Art Museum, Worcester, Massachusetts, for allowing the opportunity to examine the *Holy Family* and Stephan Kornhauser for sending us information on *The Battle of Orlando and Rodomonte* in the Wadsworth Athenaeum, Hartford, Connecticut.

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3. *The Battle of Orlando and Rodomonte*, c. 1525. Wadsworth Athenaeum, Hartford, CT. Canvas, 0.82 × 1.37 m. 1949-81.
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## Abstract

Restoration of a large 16th-century altarpiece was carried out in the Frans Halsmuseum between 1989 and 1991. The wings were commissioned from Maarten van Heemskerck in 1546, and a later centrepiece was commissioned from Cornelis Cornelisz. van Haarlem in 1590. Treatment was preceded by a preliminary investigation of the materials, techniques, and conditions of the paintings, carried out by an interdisciplinary team. Since the altarpiece was a civic commission, archival sources recorded the provenances of the paintings and frames, as well as the sources of the materials used and the division of labour. Scientific examination of the paintings was carried out using such techniques as stereomicroscopy, stereo and normal X-radiography, and paint sample analysis. A comparison of Cornelis van Haarlem's centrepiece, with the wings which Van Heemskerck had painted less than fifty years earlier, showed that important technical developments had taken place.

## Keywords

Maarten van Heemskerck, Cornelis Cornelisz. van Haarlem, paintings, paintings conservation, scientific examination

## Technical Developments in a 16th-Century Netherlandish Altarpiece by Maarten van Heemskerck and Cornelis Cornelisz. van Haarlem

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## Introduction

The so-called "Drapeniers altaar", the altarpiece of the wool trader's guild in the Saint Bavo Cathedral in Haarlem, incorporates wings by Maarten van Heemskerck (1498–1574) and a later centrepiece by Cornelis Cornelisz. van Haarlem (1562–1638). Recent restoration of the paintings in the Frans Halsmuseum in Haarlem was sponsored by the Dutch Ministry of Culture.

## A brief history of the altarpiece

Archival sources provide valuable background information about the altarpiece (1). A contract dated 4 January 1546, informs us that Maarten van Heemskerck was commissioned to provide two innermost doors ("binnenste deuren") for the "Drapeniers altaar," a statement which suggests that the altarpiece could have been a polyptych. The outsides were to depict "The Annunciation," the inside facing North "The Nativity," and adjacent "The Adoration of the Kings." Van Heemskerck was also to deliver painted and gilded frames. The commission was completed in one and a half years. The final payment was made on 8 January 1548, four months after completion. The shutters were added to an unknown centrepiece, and the new ensemble decorated the wool trader's altar in the Saint Bavo Cathedral, Haarlem for approximately thirty years. Damages in Mary's gown on the left wing exterior, uncovered during the recent restoration, were possibly caused by a lamp which, in certain periods, reportedly burnt overnight by the altarpiece.

The original centrepiece of the "Drapeniers altaar" was destroyed at some time in the last quarter of the sixteenth century, prior to the Reformation in 1578. The surviving wings were moved to a Dominican cloister, which was later converted into the guest quarters of the city governor, the so-called "Prinsenhof" in the townhall.

In 1590, the city council commissioned Cornelis Cornelisz. van Haarlem to paint a new centrepiece, "The Massacre of the Innocents." In order to harmonize with the new, almost square centrepiece, the lobed side panels were filled out into a rectangle with additions by Cornelisz. van Haarlem. The city arranged for a "stofeerder" to modify, repaint, and regild the frames, rather than leaving the frames to the responsibility of the painter (as in the earlier Van Heemskerck commission). Cornelis Cornelisz. Prins received payments in 1590 and 1591 for the cost of materials and labour on the frames. The commissioner, rather than the painter, also provided the linen used as a painting support. A bill from 1590 records canvas purchased from the dealer Quirijn Janssen, to be used for a number of paintings by Cornelis van Haarlem.

In 1804, the "Drapeniers altaar" was sold to the state, the Batavian Republic, in partial exchange for return of the townhall bought in 1800. As national property, the altarpiece came to hang in the "Nationale Konst-Gallerij" and later in Het Mauritshuis, The Hague. After 1809, the centrepiece and wings were separated until the middle of this century. Around 1955, "The Massacre" was reunited with the Van Heemskerck wings, which had already come on permanent loan to the Frans Halsmuseum in 1917. A new frame was made for "The Massacre" and the frames of the wings were adapted and redecorated to

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Figure 1. Photo assembly of the "Drapeniers altaar." Wings by Maerten van Heemskerck ( $2.95 \times 1.43\text{m}$ ), depicting "The Annunciation" on the outside and "The Adoration of the Shepherds" (left) and "The Adoration of the Kings" (right) on the inside, 1546–1547. Centrepiece by Cornelis Cornelisz. van Haarlem ( $2.68 \times 2.57\text{m}$ ), depicting "The Massacre of the Innocents."



match. A photo assembly of the "Drapeniers altaar" altarpiece is shown in Figure 1.

#### Technical examination of the wings by Maarten van Heemskerck:

##### *The panel supports*

Van Heemskerck would have obtained the large oak panel supports, ready assembled in their frames, from a specialist carpenter. Each panel comprises five



vertical planks, symmetrically arranged, with the narrowest plank in the centre. Slightly different plank widths are combined to fill out each panel. The planks were butt-joined and glued, with no additional reinforcement, and the assembled panels were evened to a thickness of ca. 6–8 mm by tooling. The edges of the panels were bevelled, and extended slightly into the painted area to slot into the frame rebates.

The small panels added by Cornelisz. van Haarlem comprise a single plank, with the grain oriented horizontally, in contrast to the main panels.

#### *The frames*

The lobed frames provided by Van Heemskerck were Gothic in style, with foliate ornaments on the cusps. In 1590–91, Cornelis Prins converted the frames into a rectangular format to receive the additions by Cornelis van Haarlem. Examinations suggested that the short sides have been extended to meet horizontal members added above the arches, where the frame shows a different inner profile. The decoration of the Gothic frames was apparently removed before the modified frames were repainted and regilded, since cleaning tests and paint sample cross sections showed that the oldest decorative layers present on all parts of the modified frames are the same. The main surfaces were painted with a thin layer of bone black bound in a little oil medium, applied on a chalk and glue ground, and the profiles and ornaments were oil gilded. Paint samples confirmed that paint applied to the added panels by Cornelis van Haarlem had run over onto the adjacent frame, and visa versa, confirming that the black decoration of the frame was contemporary.

Examination revealed up to ten layers of overpaint (ground and paint layers) on original parts of the frames, which had been modified around 1955 to match the new frame of the reunited "Massacre."

#### *The ground layers*

The presence of a barbe and the bare edges of the main panels suggest that they were primed in their frames, perhaps before delivery to Van Heemskerck. The rather thin chalk-glue ground (0–40  $\mu\text{m}$  in paint samples) was made less absorbent by a lead white in oil imprimatura, brushed streakily on top (2). No attempt was made to fill a long damaged area in the ground that was present across the two left planks in "The Nativity" before execution of the painting.

The added panels by Cornelis van Haarlem were prepared in the modified frames with a thickly applied lead white and oil ground. The surrounding frames preserve a matching barbe. The single ground layer, apparent in paint samples, was roughly brushed onto the panels.

#### *Underdrawing*

Underdrawing was only detected in the architectural backgrounds on the wing exteriors. Some lines have been incised into the wet ground layer, either along a straight edge or using a compass for the arches. Other black, apparently chalk, lines were drawn on top of the streaky imprimatura, with some cursory hatching. The lines of the underdrawing stop short of the main figures, suggesting that their position was already fixed. The underdrawing was not always followed exactly in the finished design, as in the floor of "The Annunciation." A possible reason for confining dark lines of underdrawing to the backgrounds only was the knowledge that increased transparency of overlying paint layers could cause them to become disturbing, as can often be observed in figures by Jan van Scorel, Van Heemskerck's teacher in the period 1527–30.

#### *The paint layers*

Most areas of the composition have been laid in using pinkish through red to brown paint; the paint samples contain lead white, organic red, and sometimes inorganic red. Translucent red underpaint is visible around the flesh contours,

which a paint sample from the edge of Angel Gabriel's hand showed to be a thin layer (ca.  $6\mu\text{m}$ ) containing lead white, vermilion and a few particles of red lake. Translucent brown underpaint, streakily applied, is occasionally exposed in the background of *The Annunciation*. The various shades of underpaint applied on the white imprimatura, would have broadly differentiated tonal areas. Paint samples revealed that the warm underpaint is sometimes covered by opaque paint layers, as in the yellow draperies, or is absent, as in the blue draperies. Flesh-coloured undermodelling has been observed in three other painting by Van Heemskerck, but applied directly on the chalk ground where its position in the layer structure resembles an imprimatura (3).

Although underdrawing was not detected by technical examination, the complex figural compositions of the "Nativity" and "Adoration" scenes must have been carefully planned. Colour areas have been carefully reserved, and overlaps occur only where there are slight pentimenti. Most apparent are the changes in position of the heads and hands, so that they overlap the dark backgrounds made visible by the increased translucency of the flesh paint on top. A more major pentimento occurs by the ox in "The Adoration of the Kings;" a figure in a blue (azurite) costume, whose outline exactly follows that of the man in dark brown clothing placed directly above, underlies the ox. Technical examination did not provide evidence for an earlier position of the ox.

In contrast to Van Heemskerck's inevitable procedure of leaving figures in reserve in the backgrounds, Cornelis van Haarlem simply paints them on top. This difference is apparent in comparing Van Heemskerck's angels and putti in "The Nativity", with those added by Cornelis van Haarlem above.

Paint analysis showed that Van Heemskerck used a limited palette of mainly traditional pigments. These include the unpopular poisonous pigment, orpiment, identified in the Angel Gabriel's apron (4). Lead tin yellow was identified in other yellow costumes. Azurite was identified in several places, including Mary's blue drapery in "The Adoration of the Kings," despite the fact that it was reportedly scarce and expensive in this period due to repeated invasions of Hungary from where it was imported (5).

Most surprising is Van Heemskerck's use of smalt (a pigment which appears to have been only very recently introduced in North Netherlandish paintings) for the larger area of Mary's blue drapery in "The Annunciation." Shadows were glazed over an opaque, light blue underpaint which contained smalt mixed with various quantities of lead white. Microscopic examination of damages revealed detailed undermodelling. Presumably, unlike painters at the end of the century, Van Heemskerck was not yet aware of the property of smalt to discolour to a greyish brown when used with a lot of binding medium, as has occurred in the glazed shadows (6).

Other original colour effects have been lost due to darkening of glazes. Copper resinate glazes applied over a light blue underpaint (containing azurite and lead white) to provide a cool green colour in the pageboy's gown in "The Adoration of the Kings" have discoloured brown and become opaque under the influence of light and oxygen (7). The purple colour of the drapery on which Mary kneels in "The Annunciation" was created by applying red lake glazes over a blue layer which chiefly contains azurite, mixed with a little red lake and black pigment. This effect is hidden by glazes containing fine black on top, which have darkened due to discolouration of the oil binding medium.

Surface examination suggests the use of black pigment to deepen shadows in other draperies, as in the red velvet gown of the king by the right edge in "The Adoration," where striking contrasts are achieved by the addition of lead white in the highlights (8). This opaque method of colour modelling extends the tonal range provided by the traditional technique, as described in Mary's blue (smalt) gown, of applying coloured glazes over a light underpaint. It also permits a more versatile application of paint, so that Van Heemskerck was able to evoke the quality of velvet by contrasting sharply delineated highlights with softly blended shadows, swept with a soft brush or other feathered implement.



### Technical examination of the centre-piece by Cornelis Cornelisz. van Haarlem:

#### *The canvas support*

Cornelis van Haarlem was supplied with canvas to paint "The Massacre of the Innocents," despite the fact that the existing wings by Van Heemskerck were on panel. He appears to have favoured lightweight canvas for large-scale history paintings, completing another large canvas depicting "The Massacre" in the same year as he obtained this commission (9). Cornelis Cornelisz.'s large canvas supports were made by sewing strips together, in this case three vertical strips. Examination suggested that a length of canvas measuring ca. 102 cm wide had been used, the measurement of the widest strip including the intact seams. This width of canvas was usually sold for domestic purposes. Only in the 17th century were painters in Haarlem able to obtain large widths of canvas for their single-piece painting supports. The canvas is finely woven with an average of 20 warp (vertical) and 17.5 weft threads threads per cm.

#### *The ground layer*

The canvas was prepared with a cool grey ground containing a complex mixture of pigments: lead white, lamp black, red and brown ochre, and very little blue (apparently smalt) bound in oil medium. A single layer is apparent in paint samples, which has been streakily applied using sweeping brush strokes. Cornelis van Haarlem's innovatory use of large canvases prepared with coloured grounds was presumably inspired by Venetian examples. He experimented, using not only grey but also red grounds, as in his "Wedding of Peleus and Thetis" in the Frans Halsmuseum, painted around 1593.

#### *The paint layers*

Examination did not reveal underdrawing using black pigment, or any other material. The composition has been thinly laid in on the light grey ground, using various shades of white through cool grey to brownish grey paint. Flaking losses revealed that this monochrome underpaint suggested detailed modelling, which has been closely followed in the finished design. Only the distant figures were not planned at the underpaint stage, but were added later over the finished backgrounds. Cornelis van Haarlem's practice of copying plaster casts of antique sculpture, or the tradition of grisaille painting in its own right, may have inspired this procedure. Van Heemskerck had already experimented with monochrome undermodelling to modify the white grounds of his paintings on panel, as in the wings of the "Drapeniers altaar."

The grisaille underpaint provides a basis for the various flesh tones which Van Mander so admired (10). In the cool tones of female and dead infant flesh, it shows through light flesh paint applied thinly on top to exploit the so-called "turbid medium effect," whereby a light colour laid over a dark one appears cooler because of the scattering of blue light and the absorption of red and yellow. In addition, a little blue pigment has been mixed into the cool grey shadows of the dead child in the middle distance. On the other hand, monochrome underpaint is often absent in the warm pink flesh tones, as in the arm of the standing man by the right edge, where the thick layer of flesh paint would have covered it anyway. The grisaille underpaint is strongly visible through the thinly-painted grey background architecture.

Cornelis van Haarlem's painting procedure was systematic; paint cross sections showed an elaborate build up of layers with many separate stages. Following the grisaille stage, the principal naked figures were completed before painting their costumes on top. Blue dresses were laid in using opaque grey underpaint that contained smalt or black mixed with lead white; this covered the flesh paint. Azurite was used in the main paint layers, with patterning finally detailed on top. In the early 17th century, Hendrick Goltzius used a simpler technique for painting draperies directly on the cool grey grounds (11).

Cornelis van Haarlem applied final paint layers using brush strokes hatched around forms to blend adjacent wet areas of paint. Together with scumbled

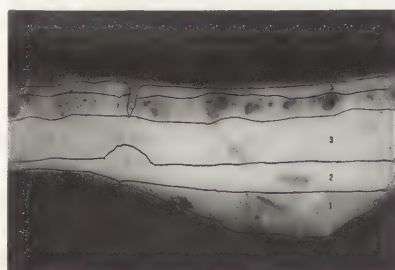


Figure 2. Cornelis Cornelisz. van Haarlem, "The Massacre of the Innocents," 1591. Cross section of paint sample from the blue clothing of the woman in the right foreground, showing an elaborate build up. The figure was painted naked before adding clothes on top. Underpaint for the flesh is absent in this sample. The layers are as follows: 1) the grey ground, 2) pink flesh, 3) light blue underpaint (containing smalt) for the blue clothing, 4) main paint layer (containing azurite) of the blue clothing, 5) grey stripe in the clothing, and 6) varnish layer(s).

contours, this provided a soft chiaroscuro effect and a natural rendering of form, in contrast to the abrupt modelling transitions which Van Mander criticised in paintings by Van Heemskerck (12).

### Conclusion

This technical examination of two altarpiece wings by Maarten van Heemskerck supports the view that he was a somewhat experimental painter who varied his technique (13). In particular, the combination of warm undermodelling applied on a white imprimatura does not reoccur in the small group of panel paintings by Van Heemskerck examined to date. This examination also revealed an earlier example of Van Heemskerck's use of the unexpected pigments orpiment and smalt. Van Heemskerck shows a transitional technique, combining traditional glazes with a new method of colour modelling, using opaque paint mixtures which exploit different textures of paint application. These innovations, as well as the use of a monochrome undermodelling, are developed in Cornelis Cornelisz. van Haarlem's new centrepiece, "The Massacre of the Innocents," painted less than fifty years later. Unprecedented in The Netherlands was Cornelis Cornelisz.'s choice of a large canvas prepared with a coloured ground for the painting support. Clearly, he was not inhibited by the nature of the commission to reconstruct an earlier altarpiece, since little concession has been paid to its original character. The Gothic frames were transformed to receive the new additions by Cornelis Cornelisz. and the original decoration apparently stripped. While Cornelis Cornelisz. borrows some motifs from the Van Heemskerck wings in his new centrepiece, he did not attempt to match their materials or painting technique, even when extending Van Heemskerck's compositions in the wings (14).

### Afterword

In order to appraise the condition of the paintings before restoration, a preliminary investigation was carried out by an interdisciplinary team in 1989. Levy-van Halm compiled archival and other sources concerning the material histories of the paintings. The painting conservators carried out surface examination of the paintings, including scrutiny with the naked eye, as well as stereomicroscopy and examination in raking, transmitted, and ultraviolet light. Tests for varnish removal were made. They examined the frame constructions and made tiny excavations to investigate overpaint layers.

Hendriks was assisted by a varying team of conservators, including E. Hermens, C. Manabe, H. van Putten, Z. Sillevius and A. Wouters for the frames. Stereo and normal X-rays were made by the Röntgen Technische Dienst, Rotterdam. Preliminary scanning with an infrared vidicon was carried out using the equipment of J.R.J. van Asperen de Boer. Paint sample cross sections were prepared and analyzed by K. Groen and M. de Keijzer (15). A treatment proposal, which took into account the research results, was accepted by an independent advisory committee established at the request of the museum director. Treatment was completed by December 1991, when the paintings were featured in an exhibition with information about the treatments and research results summarised in a museum booklet (16). This paper has focused on aspects of technique.

### Notes

1. The main sources were the archives of the Saint Bavo Cathedral and the city of Haarlem.
2. Concerning use of a lead white imprimatura, see J.R.J. van Asperen de Boer, M. Faries, and J.P. Filedt Kok, "Painting technique and workshop practice in North Netherlandish art of the sixteenth century" in *Kunst voor de beeldenstorm*, Catalogue Rijksmuseum (Amsterdam 1986), 108.
3. The paintings referred to are two early altarpiece wings, dated after 1636, and "The Delft Lamentation" of 1566. See respectively; J. Dunkerton, A. Burnstock, A. Smith, "Two Wings of an Altarpiece by Martin van Heemskerck" in *National Gallery Technical Bulletin* (London 1988), 28; and J.R.J. van Asperen de Boer, "Technical Study of some paintings by Maarten van Heemskerck", *Color and Technique in Renaissance Painting; Italy and the North* ed. M.B. Hall (New York 1987), 107.



4. For reasons why orpiment was unpopular, see J.A. van de Graaf, *Het De Mayerne manuscript als bron voor de schildertechniek van de barok* (thesis, Mijdrecht 1958), 50–51 and R. Harley, *Artists' Pigments c. 1600–1835* (New York 1982), 93–4. Orpiment has also been identified in Van Heemskerck's "Delft Lamentation", see Van Asperen de Boer et al., "Painting technique," 109.
5. C. van Mander, *Het Schilder-boeck* (Haarlem 1604), f.200v.
6. Concerning the introduction of smalt and its use in North Netherlandish paintings, see Van Asperen de Boer et al., "Painting technique," 109.
7. Copper was identified by microchemical testing, although no analysis for pine resin was done. For Van Heemskerck's earlier use of glazed greens, see Dunkerton et al., "Two Wings," 28.
8. Use of black pigment in the shadows, instead of a glaze, is also found in paintings by Pieter Aertsen, see Van Asperen de Boer et. al., "Painting technique," 108.
9. "Massacre of the Innocents," 1590, Rijksmuseum, Amsterdam, inv. no. A 128.
10. K. van Mander, *Het leven der doorluchtige Nederlandsche en enige Hoogduitsche schilders*, ed. J. de Jongh (Amsterdam 1764), f. 293r.
11. For example, see a series of three paintings by Goltzius in the Frans Halsmuseum; "Mercury" and "Minerva" of 1611, and "Hercules and Cacus" of 1613.
12. K. van Mander, *Het leven*, f. 245r.
13. Van Asperen de Boer, "A Technical Study," 111.
14. For example, for the arm of the standing man by the right edge Cornelis van Haarlem closely followed a study by Van Heemskerck, in a sketchbook which he owned.
15. Paint samples approximately 0.25 mm<sup>2</sup> in size were removed from the edges of the paintings or existing damages; 26 from the paintings by Van Heemskerck and 14 from the frames, 20 from "The Massacre" (seven in 1986 by M. de Keijzer). Paint cross-sections were prepared and provisionally examined by K. Groen at the Hamilton Kerr Institute, University of Cambridge and later examined by M. de Keijzer, Central Research Laboratory for Objects of Art and Science, Amsterdam. Paint samples were embedded in a polyester block, ground, and polished to expose the sample at one surface. Resulting cross sections were examined under the microscope in normal and long wave ultraviolet incident light. The remainder of the sample material was used for polarised light microscopy and for microchemical tests. Elements were identified using energy dispersive X-ray microanalysis of the cross sections.
16. E. Hendriks & K. Levy, *Terugkeer van de meesters; restaureren en conserveren in het Frans Halsmuseum*, ed. N. Köhler, (Haarlem 1991).

## Résumé

Le travail présenté s'appuie sur les observations faites au cours de la restauration des quatorze tableaux du Studiolo d'Urbino conservés au Louvre, sur les documents scientifiques, ainsi que sur l'examen d'une centaine de coupes stratigraphiques et l'analyse de leurs constituants au microscope électronique à balayage avec sélection des énergies de rayons X. L'article complète les informations déjà publiées et se propose de chercher des critères de différenciation entre la technique de Juste de Gand et celle de Pedro Berruguete qui a modifié et achevé les oeuvres. La majorité des pigments utilisés sont les mêmes, mais Juste emploie une laque brun-rouge qui n'appartient pas à la palette de Berruguete. Ce dernier en revanche a introduit le smalt comme pigment bleu. Les huiles utilisées par chacun sont probablement de nature différente.

## Mots clés

Italie, Juste de Gand, Berruguete, technique picturale, analyse au microscope électronique à balayage, smalt, huile

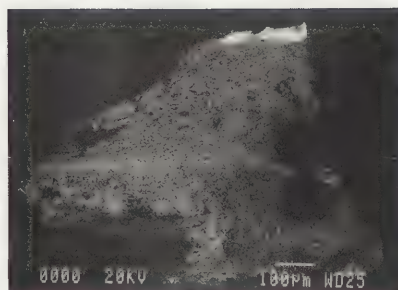


Fig. 1: Saint Augustin. Soubassement. Coupe stratigraphique.

Image en électrons rétrodiffusés montrant l'épaisseur totale de la préparation (700 micromètres). Le matériau constitutif est sur toute l'épaisseur cristallisé en fines aiguilles caractéristiques du gypse réhydraté. La préparation a été passée en deux couches séparées par un encollage.

## Les hommes illustres du Studiolo d'Urbino (Louvre). Etude de la technique picturale

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## Introduction

Après l'achèvement de son palais en 1472, le duc d'Urbino, Frédéric de Montefeltre, envisagea la décoration de son Studiolo avec des portraits d'hommes illustres. Très admiratif des oeuvres peintes précédemment à l'huile par Piero della Francesca, il rechercha un peintre maîtrisant cette technique, inhabituelle pour l'Italie de l'époque.

Il retint le flamand Juste de Gand qui établit le schéma général du décor; mais certaines différences de facture ont toujours intrigué les historiens de l'art qui ont pensé à la collaboration de plusieurs peintres.

A l'occasion de la restauration des quatorze portraits conservés au Louvre, et après l'établissement d'un dossier scientifique complet, Nicole Reynaud et Claudie Ressort ont reconsidéré les problèmes d'attribution et ont démontré que la décoration avait été faite en deux campagnes, l'une dirigée par Juste de Gand et l'autre très probablement par le peintre espagnol Pedro Berruguete (1-4).

Nous avons déjà publié un compte rendu de la restauration accompagné de quelques indications techniques (5). Le présent article complète les informations d'ordre scientifique, recherche des critères de différenciation entre les artistes, et discute la cohérence des résultats exposés avec les attributions proposées en renvoyant à l'étude de la Revue du Louvre (4). Ce travail a pris en compte l'observation des oeuvres en cours de restauration, l'examen des documents scientifiques, l'étude stratigraphique d'une centaine de coupes ainsi que l'analyse de leurs constituants. Tous les résultats détaillés ne peuvent pas être présentés ici, mais le tableau récapitulatif en annexe répertorie les stratigraphies et analyses au microscope électronique à balayage (6) des prélèvements effectués sur sept portraits dans des zones où les deux peintres sont intervenus.

## Préparation

Sur les panneaux de peuplier, entre le bois et la préparation, des bandes de toile fine sont visibles dans des lacunes profondes et sur certaines radiographies.

Sur les quatorze tableaux, la préparation, qui semble moyennement épaisse à l'examen direct, est constituée de sulfate de calcium avec de la colle (7). L'image de la préparation de *Saint Augustin* en électrons rétrodiffusés est homogène et correspond à celle du "gesso sottile" (voir Fig.1); les deux diffractions de rayons X effectuées, l'une près du support, l'autre près de la couche picturale, confirment la présence uniquement de gypse. Le peintre a ainsi respecté les usages pratiqués dans les Marches à cette époque (8).

En surface de cette préparation blanche, Juste de Gand, selon l'usage flamand, a posé une couche à l'huile pigmentée que l'on appellera impression (9, 10).

Cette couche est perceptible à l'examen direct du tableau sur presque toutes les oeuvres (11). On la perçoit en lumière rasante à travers les différentes plages colorées parce que le passage de la brosse, entraînant le blanc de plomb broyé un peu grossièrement, a laissé un léger relief strié; de couleur brun clair, elle est visible dans quelques zones réservées et dans les usures des carnations.

Elle n'est pas identique d'une coupe à l'autre d'un même portrait. Parfois très mince et à peine visible (voir Fig.2), elle peut atteindre 15 micromètres sur



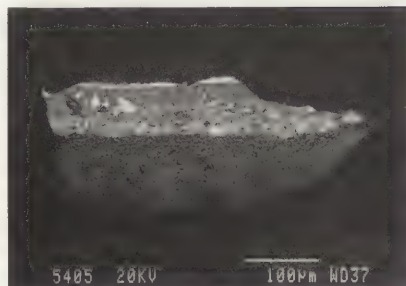


Fig. 2: Vittorino de Feltre. Tenture rose. Coupe stratigraphique.

Image en électrons rétrodiffusés montrant sur la préparation en gypse, cristallisé en aiguilles, une très mince impression à peine visible d'épaisseur légèrement irrégulière, sous la tenture verte passée en deux couches épaisses sans glacis de surface. La couche rose, peinte par Berruguete, est très mince.

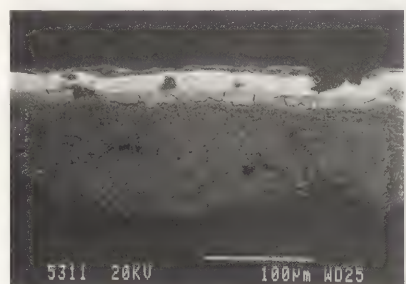


Fig. 3: Pietro d'Abano. Robe rouge. Coupe stratigraphique.

Image en électrons rétrodiffusés montrant sur la préparation en gypse, l'impression épaisse, peu chargée en blanc de plomb à gros broyage. La couche rouge obtenue par mélange de vermillon et de blanc de plomb contient quelques gros grains de laque rouge. La couche de surface n'est pas originale.

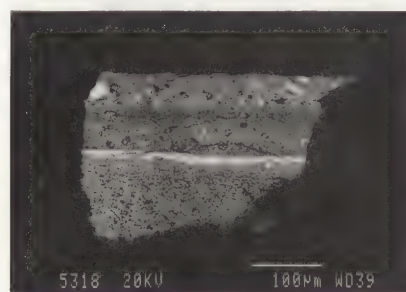


Fig. 4: Virgile. Livre vert. Coupe stratigraphique.

Image en électrons rétrodiffusés montrant sur la préparation en gypse, une impression assez épaisse et chargée en blanc de plomb. Un glacis épais vert foncé au cuivre est posé ensuite avant une couche verte plus opaque.

certaines échantillons (voir Fig.3). L'observation en fluorescence sous lumière U.V. en améliore parfois la perception. L'image en électrons rétrodiffusés permet d'apprécier la charge pigmentaire (voir Fig. 3,4) qui varie d'une coupe à l'autre et les dimensions des grains du blanc de plomb (voir Fig.2), mais sur de nombreux clichés elle n'est pas perceptible. La microanalyse de rayons X met en évidence une couche contenant du blanc de plomb en mélange avec une faible quantité de carbonate de calcium.

### Dessin

Le dessin sous-jacent a été tout particulièrement étudié pour les rapprochements stylistiques intéressants qu'il permet. Les documents déjà publiés (4) mettent en évidence la différence entre le trait initial de Juste de Gand, qui a conçu la composition, et l'exécution finale de la main du second artiste, qui n'a pas toujours respecté cette mise en place.

Ce dessin est visible à l'observation directe en raison des usures ou de la transparence accrue de l'huile.

Il est aussi décelé sur les photographies en infra-rouge, les réflectographies et sur près de 25 coupes stratigraphiques. Les traits de mise en place sont plus ou moins épais; des hachures minces et serrées, d'autres plus larges et plus noires et quelques lavis sombres préparent les modelés. Ce dessin à la détrempe protéinique (9) est posé sur la préparation blanche comme on le voit nettement sur quelques coupes et sur certains détails montrant que le passage de l'impression a entraîné les grains noirs du dessin dans le sens de la brosse.

### Couche picturale

Aucune stratigraphie n'a mis en évidence un vernis entre les deux phases de l'exécution, et la distinction de matière picturale entre les deux peintres n'a pas pu se faire selon ce critère. La présence de réserves pour les visages et pour les mains, très nette en radiographie (voir Fig.5B) et l'état inachevé dans lequel Juste a laissé, non pas un tableau mais la plupart d'entre eux, suggère une certaine répartition du travail, un aide ayant pu avancer les parties secondaires pour permettre au Maître de terminer plus vite le Studiolo (12).

L'étude de la matière picturale en radiographie permet, en effet, de constater des fractures assez différentes; les coups de brosse sont très apparents, en particulier dans les fonds d'architecture (voir Fig.5B) et les soubassements (voir Fig.6B), zones exécutées lors de la première campagne, alors que les visages de *Saint Augustin* et de *Saint Jérôme* ou les mains de *Saint Thomas* ainsi que certains vêtements peints par Juste de Gand sont plus transparents aux rayons X et réalisés avec une technique plus soignée.

Bien que ponctuée de rehauts, la matière utilisée par Berruguete apparaît faiblement opaque avec peu de coups de brosse visibles (voir Fig.5B). On peut en particulier remarquer que la matière couvrant les réserves laissées par Juste de Gand, impressionne très peu le film radiographique (main d'*Aristote*, atlantes (voir Fig.6B), robe de *Pietro d'Abano*, chapeau de *Solon*) et que les rehauts des soubassements sont beaucoup moins opaques que les parties basses exécutées précédemment.

La connaissance de la palette des deux peintres et les modalités d'application des couleurs contribuent aussi à mieux définir les origines culturelles des artistes.

Juste de Gand a peint d'un **bleu** vif les manches de *Sénèque* et de *Platon* ainsi que la robe de *Ptolémée* et le livre de *Vittorino de Feltre*. La matière moyennement dense en radiographie garde légèrement la marque de la brosse qui souligne les plis. Le pigment bleu identifié est le lapis-lazuli, rompu de blanc et utilisé sans sous-couche. La coiffe portée par le personnage prévu antérieurement à *Sixte IV* est exécutée aussi avec du lapis-lazuli. Certains accessoires peints par Juste contiennent de l'azurite comme le livre de *Dante*, mais son emploi est minoritaire.

Berruguete a préféré mêler le lapis-lazuli à d'autres pigments pour obtenir des teintes mauves comme le vêtement d'*Aristote* ou la robe de *Sixte IV*. La détection d'un peu de smalt constitue un résultat intéressant d'un double point de vue. Ce





Fig. 5A: Virgile. Détail de l'angle supérieur gauche en lumière rasante.

Sur le cliché on observe le vêtement de couleur rouge sombre et l'étroite zone délimitée par un léger relief qui correspond à la première silhouette peinte primitivement en rose puis cachée par le fond d'architecture actuel.

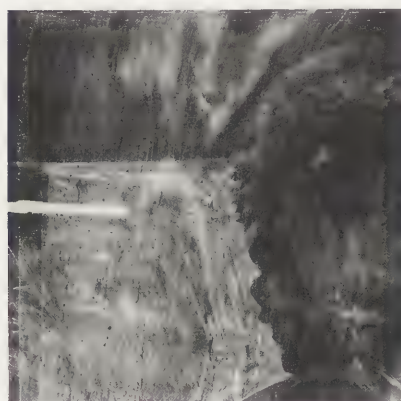


Fig. 5B: Virgile. Détail de l'angle supérieur gauche en radiographie.

Le fond d'architecture présente des coups de pinceau désordonnés très opaques qui contrastent avec le vêtement rose peint aussi lors de la première campagne. Lors de la seconde phase de travail, Berruguete a peint le visage laissé en réserve d'une façon légère avec quelques rehauts, et rétréci l'épaule du vêtement avec une matière peu opaque qui recouvre aussi le fond d'architecture.

pigment a été identifié dans le liseré blanc bordant à droite le portrait d'*Aristote*, dans la reprise du soubassement de *Dante* et dans le chapeau de *Solon*. Ces localisations correspondent à la seconde campagne, ce qui attribue à Pedro Berruguete cette innovation qui constitue une référence précoce de l'utilisation du smalt (13).

La couleur **rouge** est largement représentée sur l'ensemble des tableaux tant pour les tentures que pour les vêtements. Une trentaine de coupes concernent cette couleur dont les nuances sont obtenues à partir de vermillon et de différentes laques. Le vermillon semble avoir été particulièrement affecté par Juste de Gand qui a peint dans cette teinte, non seulement le vêtement de *Saint Jérôme* et le chapeau de *Bessarion* comme le veut la tradition, mais aussi une partie des vêtements de *Vittorino de Feltre* et d'*Aristote*, aujourd'hui cachés, l'intérieur du manteau de *Saint Augustin* et les tentures derrière *Sénèque* et *Platon*. On observe une certaine déficience technique dans la plupart de ces rouges qui présentent des boursoffures inhabituelles dues probablement à une concentration pigmentaire volumique excessive et à un mauvais mélange du liant avec le pigment comme le suggère l'observation en fluorescence sous U.V des coupes.

Ces zones sont opaques aux rayons X; la modulation y est peu importante sur la radiographie, car elle est donnée en partie par des couches transparentes aux rayons X (couche noire sous-jacente et glacis de surface assez mince en laque rouge carmin). On constate, par contraste, combien le vêtement de *Pietro d'Abano*, la tenture et le livre de *Solon*, peints par Berruguete, sont peu opaques aux rayons X. Les couches constitutives, d'épaisseur comparable, contiennent pourtant du vermillon et du blanc de plomb en mélange avec un peu d'ocre ou de laque (voir Fig.3), mais c'est la faible concentration en pigments qui explique probablement la différence constatée sur la radiographie et confirmée par l'analyse (14). On note aussi le bon état de conservation de ces rouges et l'absence de lavis dans les ombres. Juste de Gand a fait par ailleurs le choix d'une laque brun rouge fixée sur alumine qui se manifeste par une vive fluorescence orangée sous U.V (15). En glacis ou en mélange avec du blanc de plomb, il a peint ainsi la tunique et la coiffe de *Dante* ainsi que le col du mantelet de *Pietro d'Abano*. Même protégée de la lumière comme sous les feuilles de laurier de la coiffe de *Dante*, cette laque présente sur coupe une couleur peu vive assez inhabituelle. D'autres zones étaient peintes avec cette même laque mélangée à du blanc de plomb. L'analyse et l'observation sous U.V semblent le démontrer pour la première robe d'*Aristote* et pour l'état initial des intérieurs de manche de *Ptolémée*.

Berruguete a fait un usage très large d'une autre laque rouge foncée, non fluorescente sous U.V. Il reprend avec cette couleur certaines tentures et certains livres déjà peints en rouge, le vêtement de *Virgile* (voir fig.5A), le col et les intérieurs des manches de *Ptolémée*.

La robe de *Sénèque*, **jaune** avec des ombres vertes, peinte lors de la première campagne, est d'une teinte peu vive, mais l'analyse n'a décelé que du jaune de plomb et d'étain de variété I (16). Il est probable que la décoration du Studiolo comportait initialement un plus grand nombre de plages jaunes. En effet le manteau de *Platon* et celui de *Solon*, actuellement à dominante verte, étaient construits de façon assez semblable à la robe de *Sénèque* avec délimitation des zones vertes par le dessin sous-jacent. Les plages peintes dans un premier temps avec du jaune de plomb et d'étain sont décelables sur la radiographie par une opacité élevée, différente de celle des zones vertes primitives en glacis directement sur la préparation comme la partie senestre du vêtement de *Platon*. Berruguete a laissé telle quelle la robe de *Sénèque*, mais a très probablement modifié le manteau de *Platon* par ajout d'un mince glacis vert et celui de *Solon* en le reprenant d'une façon plus importante par pose d'une couche verdâtre et d'un glacis vert.

Les **verts** d'un ton éclatant sont largement représentés et sont en général bien conservés. L'analyse sur une vingtaine de coupes décèle uniquement du cuivre comme élément majeur quel que soit le peintre. Des analyses individuelles de grain pigmentaire mettent parfois en évidence d'autres éléments comme le chlore, le soufre et le zinc (17), mais cela ne semble pas être un critère de différenciation entre les artistes. Il s'agit probablement, le plus souvent, d'un vert amorphe de type "résinate de cuivre" (18). L'analyse élémentaire des glacis vert foncé met





Fig. 6A: Platon. Détail de l'angle inférieur droit en lumière rasante.

Sur le cliché on observe le soubassement actuel qui, pour ce tableau, a été repris sans qu'il y ait rehaussement. Des craquelures prématurées sont visibles dans les mains et sur la tranche du livre.

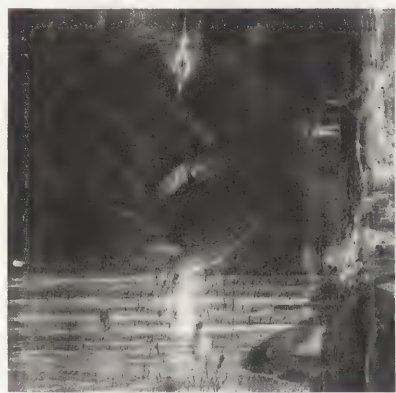


Fig. 6B: Platon. Détail de l'angle inférieur droit en radiographie.

Le soubassement peint d'abord avec une matière opaque, comportant un atlante laissé en réserve, a été recouvert par Berruguete d'une matière peu opaque aux rayons X.

en évidence en plus du cuivre, un peu de calcium pour ceux qui appartiennent à la première campagne d'exécution.

Les couleurs vertes mélangées de blanc semblent en général être le fait de Juste de Gand (18), mais dans certains cas le peintre éclaircit le vert au cuivre par du jaune de plomb et d'étain de type I comme le fait le plus souvent Berruguete. On peut remarquer le peu d'usage que Juste de Gand a fait des glacis de vert au cuivre. A-t-il peint les tentures en laissant inachevée la couche de surface? ou s'agit-il d'une technique adaptée à un style décoratif? Il est sûr que la tenture derrière *Vittorino de Feltre* de couleur verte à l'origine ne comporte pas de glacis général de surface (voir Fig.2) et que l'on ne peut pas attribuer son absence à une usure en se fondant sur cet exemple. De même la robe de *Sénèque* n'avait pas un glacis vert général d'après l'observation de la zone du vêtement cachée sous la partie du livre ajoutée par Berruguete. Dans certains cas la couche vert foncé, posée sur la préparation (voir Fig.4), se trouve sous une couleur plus claire, peinte par la suite.

L'étude des **liants** par coloration spécifique (9) a montré que toutes les couches colorées comportaient principalement de l'huile. Des analyses en chromatographie en phase gazeuse (19) ont été faites d'abord sur deux tableaux. Pour les échantillons, l'un bleu et l'autre vert, issus de *Platon*, le rapport des concentrations en acide palmitique et stéarique est de 1,8; pour les cinq échantillons de *Solon* le rapport est plus élevé quelle que soit la couleur (entre 2,6 et 3,5). D'après l'étude stratigraphique des prélèvements correspondant aux analyses, et compte tenu de l'épaisseur des couches peintes respectivement par l'un et l'autre peintre, il semble probable que Juste de Gand a utilisé de l'huile de lin et Berruguete de l'huile de noix. L'huile de lin a été détectée (20) sur trois autres tableaux dans des zones peintes sous la direction de Juste de Gand: vêtement rouge de *Saint Jérôme*, couche profonde du soubassement de *Saint Augustin*, tenture rouge de *Sénèque*.

En revanche, pour la robe de *Sixte IV* peinte par Berruguete, un rapport beaucoup plus élevé des pics d'acide identifiant plutôt de l'huile de noix a été trouvé.

L'apparition de **craquelures prématurées** dans la grande majorité des portraits (voir fig.6A) est probablement due à la conjugaison de plusieurs facteurs: siccativité insuffisante des huiles de l'époque, en particulier de celle utilisée pour l'impression, mauvaise formulation de la matière picturale, caractère inhibiteur de séchage des pigments employés dans les ombres.

En ce qui concerne la différence d'**écriture picturale**, on note que Juste de Gand rajoute des accents, peu nombreux, relativement larges et réguliers: rehauts de jaune de plomb et d'étain pour donner l'illusion de l'or dans les brocarts, trait de contour assez appuyé pour souligner les yeux.

Le style de Berruguete est au contraire graphique et spontané. De très fins traits de pinceaux clairs ou sombres, irrégulièrement appuyés et assez espacés suggèrent sourcils broussailleux, plis au coin de l'oeil, chevelures et barbes légères; les mains sont parfois cernées d'un fin trait de contour sombre, les doigts striés de petites lignes horizontales; les ongles, hâtivement esquissés par quelques rehauts noirs à peine jointifs, sont éclairés par deux ou trois touches blanches.

De même, on peut observer la différence de traitement des bijoux chez les deux peintres. Les perles attribuées à Juste de Gand sont entièrement peintes avec une matière grise dense dont les traits de pinceau circulaires sont visibles en radiographie, puis ponctués par un rehaut blanc. Celles peintes par Berruguete apparaissent comme des boules de verre: transparentes en radiographie, elles n'existent que grâce à une touche en forme de croissant suggérant le contour et à un accent de lumière au centre.

## Conclusion

Le Studiolo d'Urbino a été peint par deux peintres de culture artistique différente, aidés peut-être par des exécutants locaux, mais les matériaux utilisés sont ceux que l'on trouvait sur place. Chacun des peintres a gardé une certaine marge d'originalité: Juste de Gand a utilisé une laque brun-rouge inconnue de Ber-

Tableau récapitulatif (21).

Tableau	Lieu de prelevement	Analyse au M.E.B	Conclusion
<b>Aristote</b>	<b>I. Liseré blanc</b>		
	Stade 1. Tenture vert foncé	<b>Cu, Pb, Ca</b>	Vert au cuivre avec un peu de blanc plomb et de carbonate de calcium
	Stade 2. Robe mauve	<b>Pb, Ca, Al, Si, Fe (Si, Al, S, Na, Ca)</b>	Blanc de plomb, lapis, laque rouge, ocre
	Liseré blanc	<b>Pb (Si, Fe, As, Na, Ca, Co)</b>	Blanc de plomb et smalt
	<b>II. Vêtement mauve</b>		
	Stade 1. Robe beige rosé	<b>Pb, Ca, Al</b>	Blanc de plomb et laque brun-rouge avec un peu de carbonate de calcium
<b>Dante</b>	Manteau rouge	<b>Pb, Hg, S</b>	Vermillon et blanc de plomb
	Stade 2. Vêtement mauve	<b>Pb (Pb, Al), Si</b>	Blanc de plomb, laque rouge et lapis probable
	<b>I. Couronne de laurier</b>		
	Stade 1. Coiffe couche rose	<b>Pb (Pb, Al) (Si, Ca)</b>	Blanc de plomb et laque brun-rouge
	Couche rouge	<b>S, Ca, Al, Pb, Fe</b>	Laque brun-rouge
	Stade 2. Feuille verte	<b>Cu (Pb, Sn)</b>	Vert au cuivre et jaune de plomb et d'étain I
<b>Platon</b>	<b>II. Soubassement</b>		
	Stade 1. Soubassement beige	<b>Pb, Si, Fe, Ca</b>	Blanc de plomb avec de l'ocre
	Stade 2. Soubassement bleuté	<b>Pb (Si, Fe, Co, As) Si</b>	Blanc de plomb, smalt et divers grains
	<b>I. Tenture rouge</b>		
	Stade 1. Manteau vert foncé	<b>Cu, Ca (Pb, Sn)</b>	Vert au cuivre avec un peu de carbonate de calcium et de jaune de plomb et d'étain I
	Stade 2. Tenture rouge	<b>Pb, Al, Si, Fe</b>	Blanc de plomb, laque rouge avec un peu d'ocre
<b>Sixte IV</b>	<b>II. Manteau vert</b>		
	Stade 1. Jaune éteint	<b>Pb, Sn</b>	Jaune de plomb et d'étain I
	Stade 2. Glacis vert mince	<b>Cu, Pb, Sn</b>	Vert au cuivre avec un peu de jaune de plomb et d'étain I
	<b>I. Tenture verte</b>		
	Stade 1. Manteau ocre	<b>Fe, Al, Si, Ca, K, Mg, Pb</b>	Ocre et carbonate de calcium
	Stade 2. Tenture verte	<b>Cu, Pb</b>	Vert au cuivre
<b>Solon</b>	<b>II. Robe violine</b>		
	Stade 1. Manteau ocre	<b>Pb, Si, Al, Fe, K, Ca</b>	Ocre
	Stade 2. Robe violine	<b>Pb (Al, Si, S, Na, Ca) (Al, Pb)</b>	Blanc de plomb, lapis et laque rouge
	<b>I. Manteau vert</b>		
	Stade 1. Jaune éteint	<b>Pb, Sn, Cu</b>	Jaune de plomb et d'étain I, pas de vert visible
	Stade 2. Jaune lumineux et vert	<b>Pb, Sn, Cu</b>	Jaune de plomb et d'étain I et vert au cuivre
<b>Virgile</b>	Glacis vert	<b>Cu, Pb, Sn</b>	Vert au cuivre avec un peu de jaune de plomb et d'étain I
	<b>I. Livre vert</b>		
	Stade 1. Vert foncé	<b>Cu, Ca (Pb, Sn) Si</b>	Vert au cuivre avec un peu de carbonate de calcium et de jaune de plomb et d'étain I
	Stade 2. Vert moyen	<b>Cu (Pb, Sn)</b>	Vert au cuivre avec un peu de jaune de plomb et d'étain I
	<b>II. Vêtement rouge</b>		
	Stade 1. Vêtement rose	<b>Pb, Ca, Al</b>	Blanc de plomb avec un peu de carbonate de calcium avec de la laque rouge
	Stade 2. Vêtement rouge	<b>Al, Pb (Hg, S)</b>	Laque rouge avec quelques grains de vermillon



rugueuse qui pour sa part a innové en introduisant du smalt comme pigment bleu. Juste de Gand mélange fréquemment un peu de carbonate de calcium avec du blanc de plomb pour l'impression ou dans les glacis verts, matériau que l'on ne trouve que rarement chez Berruguete. Ce dernier mélange des ocres à des pigments plus prestigieux comme le vermillon ou le lapis et utilise une matière beaucoup plus fluide. Les huiles ayant servi de liant sont probablement de nature différente.

La comparaison des documents et des résultats des analyses faites dans les mêmes conditions sur d'autres oeuvres de Juste de Gand et de Berruguete serait nécessaire pour compléter ce travail, mais cela dépasserait le cadre de cet article.

### Remerciements

Nous tenons à remercier les nombreux collègues cités dans les notes qui ont pris une part active à ce travail ainsi que ceux qui ont permis par leur contribution sa réalisation.

### Notes et Références

- (1) La restauration a été effectuée de 1984 à 1989 au Service de Restauration des Peintures des Musées Nationaux sous la direction de S. Bergeon, puis de N. Volle.
- (2) La série des Hommes Illustres fut déposée et partagée en 1631; après plusieurs changements de collection, 14 portraits revinrent à Urbino, et les 14 autres entrèrent au Louvre sous Napoléon III.
- (3) Dossier établi par M. Solier et J. Marsac au Laboratoire de Recherche des Musées de France.
- (4) N. Reynaud, C. Ressort, "Les portraits d'hommes illustres du Studiolo d'Urbino au Louvre par Juste de Gand et Pedro Berruguete", *La Revue du Louvre et des Musées de France*, 1991, N°1, 82-113.
- (5) J. Bret, E. Martin, "Restauration et étude technique", idem précédent, 114-115.
- (6) Travail effectué par A. Duval et M. Eveno sur équipement JEOL, JSM 840. Les échantillons ont été recouverts d'une couche de carbone afin d'assurer la conduction électrique.
- (7) J. Lavalleye, "Le palais ducal d'Urbino", Les Primitifs flamands Corpus de la peinture des anciens Pays-Bas méridionaux au XV<sup>e</sup> siècle, Bruxelles (1964). D'après l'auteur, l'épaisseur de la préparation pour les oeuvres conservées à Urbino se situe entre 210 et 550 micromètres, p 91.
- (8) E. Martin, N. Sonoda, A. Duval, "Contribution à l'étude des préparations blanches des tableaux italiens sur bois", *Studies in Conservation* 37 (1992), 82-92.
- (9) D'après les tests spécifiques pratiqués. E. Martin, "Contribution à l'analyse des liants mixtes" Comité pour la conservation de l'ICOM, 5<sup>ème</sup> réunion, Zagreb, 1978/20/8.
- (10) C. Périer d'Ieteren, "Colyn de Coter et la technique picturale des peintres flamands du XV<sup>e</sup> siècle". Bruxelles (1985), p 19.
- (11) Cette couche intermédiaire n'est signalée dans l'étude de J. Lavalleye, (op. cit.) ni pour les Hommes Illustres ni pour la *Communion des Apôtres* commandée à Juste de Gand et conservée à Urbino. D'après l'observation sur place et d'après les planches de détail de l'ouvrage, elle est pourtant visible sur la majorité des oeuvres.
- (12) J. Lavalleye (op. cit. p.4) au sujet de la *Communion des Apôtres* écrit "On est en droit de retenir la possibilité sinon la probabilité d'une exécution picturale réalisée par plusieurs mains dont le travail contraste avec celui combien soigné, des Maîtres du XV<sup>ème</sup> siècle flamand.
- (13) B. Muhletheler, J. Thissen, "Smalt", *Studies in Conservation* 14 (1969), 47-61. La référence mentionnée la plus ancienne est de 1483 chez M. Pacher.  
I.C. Alexander, A. Gallone-Galassi dans "A Study of Piero della Francesca's Sacra Conversazione and its relationship to Flemish painting techniques", 8th Triennial Meeting ICOM, Sydney, 1987, 9-12, indiquent la présence de smalt sur cette oeuvre contemporaine du Studiolo.  
D. Bomford, A. Roy, A. Smith dans "The techniques of Dieric Bouts. Two paintings contrasted", *National Gallery Technical Bulletin*, 10 (1986) signalent la présence de smalt pour un Tüchlein, *La mise au tombeau*, daté du milieu du XV<sup>e</sup> siècle.
- (14) L'intensité du spectre de rayons X émis lors de l'analyse par les couches rouges à base de vermillon est nettement plus élevée pour celles de Juste de Gand que pour celles de Berruguete.
- (15) D'après la fluorescence, il est probable qu'il s'agisse de garance (et non de bois de Brésil comme indiqué précédemment, voir note 5).
- (16) E. Martin, A. Duval, "Les deux variétés de jaune de plomb et d'étain". Etude chronologique, *Studies in Conservation* 35 (1990), 17-36. Seule la variété I a été trouvée pour l'ensemble du Studiolo.

- (17) E. Martin, M. Eveno, "Contribution to the Study of old green copper pigments in easel paintings" 3ème conférence internationale A.I.P.N.D, Viterbe, 1992, 781-791.  
Des grains (Cu Cl) sont détectés dans la première tenture de Ptolémée, des grains (Cu, S, Cl) dans les secondes tentures de Ptolémée et Virgile. L'association (Cu, Zn, Sn) est mise en évidence dans la seconde tenture de Bessarion.
- (18) L'analyse en diffraction de rayons X, faite par M. Eveno en chambre de Gandolfi sur un échantillon vert de teinte moyenne issu de la tenture derrière *Saint Jérôme*, permet d'identifier du gypse et de l'hydrocérusite mais ne met en évidence ni malachite ni acétate de cuivre.
- (19) J. Mills, "The gas chromatographic Examination of paint Media", *Studies in Conservation* 11 (1966), 92-107. Les analyses ont été faites avant restauration, après dévernissage local, par J.P. Rioux.
- (20) Analyses faites par S. Colinart sur des échantillons prélevés en cours de restauration.
- (21) Sur le tableau établi en collaboration avec M. Eveno, ni la préparation, ni l'impression ni le dessin sous-jacent ne sont reportés. Les éléments entre parenthèses correspondent à des analyses de grain pigmentaire. Les éléments majeurs sont écrits en gras.



## Résumé

L'étude comparée, inédite jusqu'à ce jour de deux panneaux la *Décollation* et le *Festin d'Hérode*, conservés au Musée d'Art et d'Histoire de Genève et au Musée Mayer Van den Bergh d'Anvers, sera présentée ici. L'examen du support, de sa datation dendrochronologique, du style et de la technique picturale seront abordés successivement. Ils démontrent que leur exécution est due à un seul et même artiste, Juan de Flandes, et qu'ils appartiennent tous deux à un même retable sans doute le retable de *St-Jean-Baptiste*.

## Mots clés

Peinture, école flamande XVe s., Juan de Flandes, méthodes d'investigation scientifique, dendrochronologie, technique picturale, critique de style

## Apport des méthodes d'investigation scientifique à l'étude de deux peintures attribuées à Juan de Flandes

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Dans le cadre de l'examen scientifique des peintures flamandes du XVe siècle, il a paru intéressant d'entreprendre une étude interdisciplinaire (1) de deux panneaux attribués à Juan de Flandes, la *Décollation* (Voir Fig. 1) et le *Festin d'Hérode* (Voir Fig. 2) conservés au Musée d'Art et d'Histoire de Genève et au Musée Mayer Van den Bergh d'Anvers.

Il s'agissait de voir, d'une part, si ces oeuvres appartenaient à un même retable démembré: le retable de *St-Jean-Baptiste* qui aurait été peint pour la Chartreuse de Miraflores de 1496 à 99 par Juan Flamenco comme cela avait été relevé dans les archives du Monastère par Antonio Ponz; d'autre part, si leur style et leur technique d'exécution s'apparentaient et enfin si leurs caractéristiques se retrouvaient dans la *Naissance de St-Jean-Baptiste* conservé au Cleveland Museum of Art et dans le *Baptême du Christ* de la collection Jordan de Urries de Madrid qui aurait aussi fait partie du même ensemble.

Leur attribution à Juan de Flandes devait encore être démontrée en s'appuyant sur d'autres critères que ceux du style, les avis des historiens de l'art étant divergents, et leur date d'exécution précisée pour pouvoir les situer dans la production du Maître.

Les supports des deux oeuvres constitués de plusieurs éléments verticaux et collés à joints vifs (2) sont en chêne, exclusivement de bois de coeur débité sur quartier. Ils ont été coupés sur plusieurs côtés (3). Les revers des panneaux ont été rabottés avant l'application d'une préparation à base de gypse identique à celle des faces et sensible sous la fine couche originale de couleur translucide brun orangé qui la recouvre (4). Il reste une barbe de cette couleur dans le bord supérieur de la *Décollation*. Les deux peintures ne présentent ni barbe sur les faces, ni trace de charnière. Le *Festin* n'a pas de bord non peint tandis que ceux de la *Décollation* sont pourvus sur trois côtés d'une bordure noire non originale, le côté gauche ayant été coupé.

L'examen dendrochronologique (5) révèle qu'il s'agit de bois importés des régions avoisinant la mer Baltique (6). J. Vynckier a démontré, par ailleurs, que l'élément B du *Festin* ainsi que les deux éléments de la *Décollation* proviennent d'un même tronc, issu d'un chêne abattu au plus tôt aux environs de, sinon peu après 1484, si on tient compte d'un aubier de 15 cernes. Les éléments A et C du *Festin*, par contre, proviennent d'un autre tronc issu d'un chêne abattu au plus tôt aux environs de, sinon peu après 1488. En conclusion, pour la *Décollation* la date d'abattage remonterait aux années 1482... 1484... 1488 ou plus, pour le *Festin* aux années 1486... 1488... 1492 ou plus. Enfin le même examen dendrochronologique met en évidence un fait inattendu: les éléments A et C du *Festin* proviennent du même tronc que celui qui a livré tous les éléments constitutifs des panneaux de la *Nativité* et de la *Piéta* du retable de la *Vierge* conservé à la Capilla Real de Grenade (7).



Fig. 1 La *Décollation* de Saint Jean-Baptiste, Juan de Flandes, ensemble. Musée d'Art et d'Histoire de Genève.

\* Auteur à qui la correspondance devrait être adressée.





Fig. 2 Le Festin d'Hérode, Juan de Flandes, ensemble. Musée Mayer Van den Bergh, Anvers.

Le fait qu'un élément du *Festin* ainsi que les deux éléments de la *Décollation* soient issus d'un même tronc d'arbre souligne que les deux oeuvres auraient appartenu à un même atelier de peinture et auraient été exécutées dans un même laps de temps, à savoir dans la dernière décennie du XVe siècle si on tient compte du temps de séchage du bois. Nous reviendrons sur ce problème de datation dans les conclusions.

La *Décollation* (Voir Fig. 1) et le *Festin d'Hérode* (Voir Fig. 2) présentent des analogies stylistiques évidentes, partiellement perçues par les auteurs antérieurs, mais jamais démontrées, et toutes propres à la manière de Juan de Flandes.

On retrouve une même organisation générale de la composition et une même insertion des personnages à l'espace, figés dans leur isolement à l'avant plan de la scène. Le style des figures principales, aux grandes formes élancées et tendues qui évoquent, mais en plus raides, celles peintes par T. Bouts, est identique. La morphologie des visages féminins se répète (Fig. 1-2), ovale et au front bombé, à la bouche petite et charnue, à l'oreille mal dessinée et trop grande. Un même contraste apparaît entre l'aspect idéalisé du visage de Salomé et l'expressivité grimaçante du visage de St-Jean. A l'air boudeur de l'un répond l'air courroucé de l'autre. La gamme chromatique est subtile dans les deux oeuvres (robe violacée et jupon vert, coiffe translucide à reflets bleutés) et riche en tons saturés et en touches de couleurs vives dans certains détails (plat portant la tête de St-Jean, bijoux).

La technique picturale est tout-à-fait analogue. L'exécution des personnages principaux est serrée alors qu'un même relâchement et une écriture, franchement schématique par endroits, s'observe dans les parties de la composition hiérarchiquement moins importantes et dans le traitement des personnages secondaires.

Conformément à l'évolution du modelé à la fin du XVe siècle, l'exécution picturale de Juan de Flandes est plus sommaire mais aussi plus expressive que celle de ses prédécesseurs.

Elle est également novatrice par l'aspect enlevé de l'écriture faite de petites touches graphiques foncées dans les ombres ou en pâte dans les claires (Fig. 6-7a) qui rompent avec la tradition des modelés fluides et créent des effets de surface. Toutefois, ces derniers ne sont pas immédiatement perceptibles, la vision d'ensemble de la peinture étant encore celle d'une peinture lisse d'aspect traditionnel.

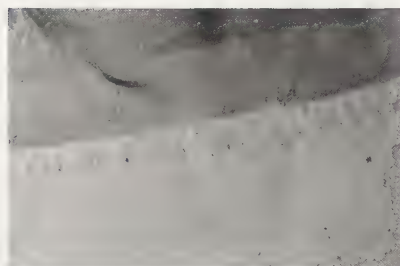


Fig. 3 La Décollation de Saint Jean-Baptiste, Juan de Flandes, détail, encolure de la chemise du bourreau.

Un examen rapproché, par contre, met en évidence une série de caractéristiques propres au maître et qui sont similaires dans les deux oeuvres. On observe ainsi une exécution lisse et en glacis du visage de Salomé mais l'apparition de courtes lignes foncées, hachurées brun-gris qui rehaussent les parties ombrées de la joue et du cou et de quelques stries en relief dans les hautes lumières et une grande variété de touches de couleur (lignes et taches) plus ou moins empâtées et de rehauts graphiques foncés pour souligner l'expressivité des visages masculins. De petits empâtements au tracé très libre mais à la facture rigoureuse sont obtenus avec un pinceau mince pour marquer certaines formes et contours des étoffes ou en animer les surfaces, par exemple dans la chemise du bourreau ou la nappe du *Festin* (Voir Fig. 3). Enfin, on note de beaux effets décoratifs dans le rendu des bijoux (pierrerie de la coiffe et pendentif) traités par juxtaposition rapide d'empâtements de couleurs vives qui ne font qu'ébaucher les formes et une pose systématique et rapide des lumières sur celles-ci (Voir Fig. 4).

L'examen d'échantillons de peinture révèle également des analogies dans la stratigraphie picturale et dans sa composition.

Les quelques échantillons prélevés dans le bord gauche coupé de la *Décollation* présentent tous la même stratigraphie: sur la préparation blanche le peintre a posé une fine couche d'impression, blanche également. Suit la mise en couleurs (nous n'avons pas trace de dessin préparatoire dans ces échantillons) à l'aide de deux couches distinctes: la première, plus opaque, la seconde pus translucide, voire composée de glacis uniquement. Cette structure semble se retrouver dans le *Festin*, quoique moins distinctement dans les quelques échantillons aussi prélevés dans les bords. La préparation se compose dans les deux cas de gypse lié à



Fig. 4 La Décollation de Saint Jean-Baptiste, Juan de Flandes, détail, bijou de Salomé.



une colle animale d'une épaisseur de 50-100 microns. La fine couche d'impression (environ 3 microns) consiste en blanc de plomb lié avec une émulsion huile-oeuf, qui toutefois n'a pu être précisé dans le *Festin*.

Dans les couleurs opaques (par exemple le dos de saint Jean-Baptiste dans la *Décollation* et le ciel dans la fenêtre droite du *Festin*) les deux couches successives se distinguent moins nettement que lorsque la deuxième couche est constituée d'un glacis. Dans ce dernier, le liant semble être à base d'huile peut-être additionnée de résine, alors que dans les couches plus opaques il est composé d'un mélange huile-oeuf.

La première couche de couleur, plus opaque, comporte des grains de noir de charbon en quantité variable selon la couleur et, sans doute, selon la fonction. Le creux d'un pli de la robe rose de saint Jean-Baptiste en comporte plus que le feuillage vert situé devant le corps de saint Jean.

Dans ce même feuillage (Voir Fig. 5bis), la première couche de couleur contient des grains d'azurite broyés très grossièrement (ces grains mesurent entre quelques microns et 50 microns dans la longueur). Ceci se remarque également dans la fenêtre droite du *Festin*. Les différentes couches de couleur, opaques ou en glacis, sont dans l'ensemble assez fines (environ 20 microns). Les pigments utilisés sont traditionnels, mais assemblés subtilement pour obtenir l'effet désiré. Une carnation par exemple (dos de saint Jean-Baptiste) est composée de blanc de plomb, de grains d'azurite, vermillon, noir de charbon et d'un colorant organique. Un rouge (creux d'un pli de la robe de saint Jean-Baptiste) est fait de vermillon, de noir de charbon et de colorant organique surmonté d'une couche de glacis (garance?). Un carreau beige du carrelage inférieur dans le *Festin*—tout comme le pavement dans la *Décollation*—sont composés de blanc de plomb additionné de noir de charbon, terre rouge et jaune.

Ces conclusions portent sur les résultats d'analyses de quelques échantillons seulement. Il convient donc de les considérer avec une certaine réserve.

Les méthodes physiques d'examen confirment à leur tour la parenté qui lie et offrent simultanément une image plus précise de l'individualité artistique, encore mal connue, de Juan de Flandes.

L'examen en réflectographie dans l'infrarouge révèle un dessin sous-jacent assez élaboré et structuré, il comprend à la fois un dessin clair de mise en place des formes, souvent soumis à des modifications, et un dessin de modelé hachuré. Dans le *Festin* (Voir Fig. 6b), l'étude du dessin est particulièrement poussée dans les vêtements de Salomé ainsi que dans les carnations de son visage et de son cou. On observe plusieurs plans de hachures entrecroisées qui annoncent les guillochages qui seront développés par Juan de Flandes dans le *retable de Palencia*. L'outil principal utilisé est un pinceau et les traits sont larges et déliés avec les dépôts de matière en bout de tracé. A certains endroits du drapé cependant, le trait a un bizarre aspect cassé qui pourrait révéler l'usage d'une plume. Il n'y a pas de traces de dessin incisé pour le carrelage. Dans la *Décollation*, le peintre s'est plus attardé sur le modelé du bourreau, en particulier dans le haut de son pantalon, au niveau de l'épaule et du bras droit tenant l'épée, ainsi que dans la lame de cette dernière. Les plans de hachures sont réalisés avec un pinceau plus fin que celui utilisé pour le dessin de mise en place. Ce dernier, quant à lui, présente une écriture très similaire à celle du *Festin* dans la largeur des tracés et dans leur souplesse.

Parmi les changements de composition, on retiendra en particulier: pour le *Festin* (Voir Fig. 6b) des modifications apportées dans la configuration de l'architecture (déplacement ou suppression des colonnes, simplification de la structure des caissons du berceau en bois, remplacement d'une fenêtre rectangulaire par l'actuel oculus) et dans la coiffe de Salomé; les bords primitivement arrondis ayant été remplacés par un galon à pampilles identique à celui de la *Décollation*. Enfin, la réflectographie dévoile la présence insoupçonnée d'un beau ciboire (Voir Fig. 5) posé sur la table. Son exécution soignée et très détaillée laisse préjuger que le peintre n'a décidé que tardivement d'abandonner ce détail.

Dans les deux oeuvres on remarque plusieurs repentirs de détails entre autres

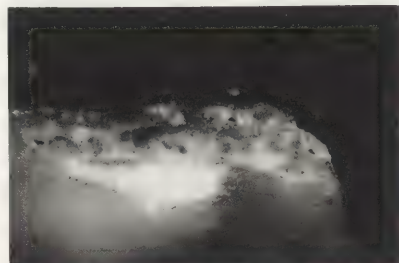


Fig. 5bis La *Décollation de Saint Jean-Baptiste*, Juan de Flandes, prélèvement dans le feuillage, bord inférieur gauche du tableau.

Stratigraphie.

- préparation blanche, gesso, 25 microns d'épaisseur
  - fine couche d'impression, blanc de plomb, 3 microns
  - couche jaune-vert, contenant des grains d'azurite et vermillon, 10 microns
  - glacis vert (résinate de cuivre?), 10 microns
- (microscope optique, gross. sur film 24 × 36 mm: 130 fois)

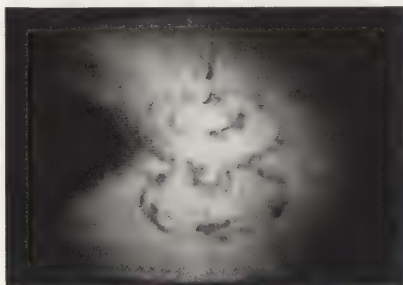


Fig. 5 Le *Festin*, Juan de Flandes, détail en réflectographie IR.

dans l'emplacement des traits des visages au stade du dessin qui procède de brèves lignes courbes (*Festin*: tête de St-Jean) ou lors d'une première phase picturale (*Festin*: profil de Salomé). Dans la *Décollation*, on notera en particulier une différence dans la position de la tête de Salomé, originellement plus inclinée vers l'avant et de ses bras plus tendus, un raccourcissement des pieds du bourreau et un déplacement de son épée. Toutes les caractéristiques précitées se retrouvent apparemment dans le dessin sous-jacent des panneaux du *retable de la Reine catholique* attribués à Juan de Flandes et exécutés dans une même fourchette chronologique 1496-1500 (8).

Enfin, il est intéressant de constater que Juan de Flandes utilise le dessin sous-jacent non seulement comme phase préparatoire à sa peinture mais aussi pour obtenir un effet pictural en surface. Dans les drapés par exemple (manche et robe de Salomé) ou dans les ombres des carnations (Voir Fig. 6b) les plis sont d'abord dessinés par un large trait qui semble avoir été ensuite recouvert d'un léger lavis de façon à créer un ton d'ombre qui est d'autant plus sensible en surface que les couches picturales de Juan de Flandes se caractérisent par leur minceur, comme l'a montré l'examen stratigraphique. Ces traits sont encore repris localement en surface et éventuellement renforcés par une ligne de couleur foncée. Cette technique de "lavis" et d'effets de surface se retrouve dans les peintures de G. David (9).

Dans les carnations des deux oeuvres (visages et mains) le dessin sous-jacent est aussi perceptible dans les ombres profondes, elles-mêmes reprises au dessus des glacis par de petites lignes hachurées et très fines de couleur brun-gris.

L'image radiographique dans l'ensemble est d'une lecture aisée (10). Une couche d'impression blanche, que l'on retrouve dans les coupes transversales, est mise sur toute la surface de la préparation, à larges coups d'une brosse sans doute assez dure vu les stries qu'elle a laissées dans la matière. Dans le *Festin* (Voir Fig. 6c), cette impression est particulièrement visible dans la figure de Salomé ainsi que dans la partie supérieure de l'architecture. Dans la *Décollation* (Voir Fig. 7c), ces coups de brosse se remarquent sous les personnages de Salomé et de sa servante, sous le plat contenant la tête de saint Jean-Baptiste, c'est-à-dire dans les parties contenant peu de blanc de plomb et étant donc plus translucides.

Dans l'ensemble, la matière picturale est mince et fluide, toutefois, Juan de Flandes recourt aux empâtements graphiques dans les hautes lumières, décoratifs dans les vêtements et les bijoux ou expressifs dans les visages, ce qui apparaît clairement sur la radiographie des deux oeuvres. La différence de technique d'exécution entre les personnages principaux et secondaires se marque par une différence d'épaisseur de la matière. Ainsi, les visages de la suivante (*Décollation*) et des souverains (*Festin*) sont plus chargés en petites touches de blanc de plomb.

L'examen de la radiographie, comme celui des réflectogrammes, révèle aussi plusieurs modifications de détails apportés cette fois entre une première et deuxième phase peinte (Voir Fig. 6-7). Ainsi, pour le *Festin*, on observe par exemple une réduction de volume de la coiffe et du manteau de Salomé et de la largeur de l'épaule du roi. Pour la *Décollation*, on note un changement dans la position du bourreau, l'échancrure élargie de sa chemise, la position de son pied qui a pivoté vers la gauche ainsi que des surélévations, rétrécissements et autres modifications dans la mise en place de l'architecture.

Des contours réservés sont utilisés à plusieurs endroits de la composition. On les observe entre autres autour du visage de la reine du *Festin* et autour de la figure du bourreau de la *Décollation* où ils sont très apparents au niveau de la tête, de l'épaule droite et des jambes. Cette pratique fréquente dans la peinture flamande du XVe siècle se justifie d'autant mieux ici que la couche picturale est très mince.

L'examen radiographique fournit encore des précisions sur l'état de conservation des deux peintures. Le *Festin* comme la *Décollation* ont été restaurés et revernés. Il n'existe pas de rapport sur les interventions de restauration. Celles-ci se situent pour la première en 1955 et en 1966 et pour la seconde en 1958. La *Décollation* a été fortement nettoyée, ce qui explique l'usure marquée de la surface picturale dans le ciel, l'architecture et les paons. L'ensemble de la composition est parsemé





Fig. 6a.b.c. *Le Festin*, Juan de Flandes, détail de la figure de Salomé en OR, IR (tube vidicon, Hamamatsu) et RX (50kV, 5 sec., 20mA, films Struturix D7 Agfa-Gevaert, 30 × 40 cm).

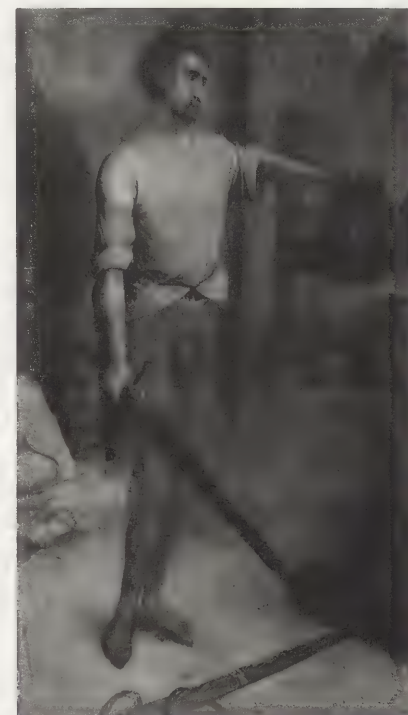


Fig. 7a.b.c. *La Décollation de Saint Jean-Baptiste*, Juan de Flandes, détail de la figure de Saint Jean en OR, IR et RX. (48kV, 2 min, 2,5mA, films Struturix D4 Agfa-Gevaert, 30 × 40 cm).



de petites lacunes tandis que des manques plus importants sont situés au-dessus de la tour et le long de la fissure qui descend jusqu'à la hauteur de la tête de Salomé. Des restes de chevilles et de clous apparaissent dans le haut du panneau. Le *Festin* présente plusieurs lacunes de faible étendue et des zones d'usures distribuées sur toute la surface. L'image radiographique montre que la partie gauche de la peinture est mieux conservée que la droite. Seules quelques lacunes y apparaissent dans la partie inférieure de la robe de Salomé et sur le mur. La partie droite, par contre, est lourdement retouchée dans l'architecture de part et d'autres du joint et dans le bas de la table et des robes en brocart des souverains.

La surface picturale a été couverte d'une épaisse couche de vernis brillant qui empêche d'apprécier à leur juste valeur les effets de texture de surface.

En conclusion, les résultats de tous ces examens confirment l'exécution des deux panneaux par un seul artiste, Juan de Flandes, et leur appartenance à un même retable.

Resituons maintenant les données fournies dans leur contexte historique pour tenter de déterminer la place qu'occupent le *Festin* et la *Décollation* dans la carrière du maître et l'ensemble duquel ils pourraient provenir.

Certains historiens d'art reconnaissent dans le *Festin* et la *Décollation* la main de Juan de Flandes, d'autres parmi lesquels C. Ishikawa (11), celle de Michel Sittow.

Pour nous, l'examen conjoint du style et de la technique d'exécution des deux oeuvres démontre à suffisance la parenté qui les lie au reste de la production de Juan de Flandes et ce qui les différencie de celle attribuée à M. Sittow (12). Le *Festin* et la *Décollation* renferment par ailleurs, au niveau de l'écriture du dessin sous-jacent et de la technique picturale, les prémisses de ce que le maître développera dans ses oeuvres plus tardives, bien documentées, comme les tableaux de Salamanque et de Palencia.

Cette discussion, d'ordre plus général, sort toutefois du contexte de cette étude centrée en ordre principal sur l'examen technologique des deux peintures.

Il nous reste encore à tenter de répondre à la question: le *Festin* et la *Décollation* faisaient-ils partie du retable de *St-Jean-Baptiste* peint pour la Chartreuse de Miraflores de 1496 à 1499, oeuvre qui aurait été commandée par Isabelle la Catholique à Juan de Flandes—si on accepte l'identification de Juan Flamenco au maître—pour orner le monastère fondé à Burgos par Ferdinand d'Aragon, son père, auquel elle était particulièrement attachée?

Les nouvelles données mises su jour permettent, semble-t-il, de retenir cette thèse. En effet, la préparation de plâtre et non de craie, comme c'est l'usage dans la peinture flamande du XVe siècle, indique que le retable a été réalisé en Espagne même, sur du bois de chêne originaire de la Baltique. La date d'abatage des arbres d'où sont issus les différents éléments constitutifs des panneaux (1484/*Décollation* et 1488/*Festin*) donne un terminus post quem de 1488 pour leur exécution. Si on ajoute les dix ans conventionnels de temps de séchage du bois, peut-être moins, la peinture a dû être commencée par Juan de Flandes vers 1498 ou un peu avant.

Enfin, l'examen dendrochronologique, en révélant que les deux panneaux sont constitués de planches issues du même arbre, prouve leur appartenance à un même ensemble réalisé dans un même atelier, d'où proviendraient aussi, selon la thèse de A. Lurie (13) les panneaux du Cleveland Museum: la *Naissance de St-Jean-Baptiste* et de la collection privée madrilène: le *Baptême du Christ*.

Pour N. Reynaud, il est très vraisemblable que le retable initial soit celui peint par "Juan Flamenco" pour la Chartreuse de Miraflores et cité par A. Ponz dans son *Viaje de España* (1776-1794), composé de 5 panneaux représentant l'histoire de St-Jean-Baptiste décrits en 1780 par l'érudit espagnol dans ses notices. Pour conforter cette thèse, N. Reynaud apporte de nouveaux éléments de réflexion (14). Selon elle, en effet, A. Ponz n'aurait pas vu le retable original mais seulement les 4 panneaux conservés et insérés dans un retable baroque en bois doré élevé en 1659 et encore en place aujourd'hui.



Le récent examen détaillé des supports, découpés sur plusieurs côtés, rabottés au dos, présentant de larges chanfreins et des traces de clous, confirme cette hypothèse. Par ailleurs, les dimensions des niches relevées alors par N. Reynaud (15) sont identiques aux mesures que présentent les panneaux dans leur état actuel. L'auteur en conclut que le *Baptême du Christ*, centre du polyptyque flamand original, aurait occupé la niche centrale du retable baroque, que la *Naissance* et la *Décollation* auraient été mises dans les niches latérales à gauche et à droite tandis que le *Festin* aurait été logé dans la niche unique occupant le sommet du retable qui est moins haute que les autres niches (16). Ceci expliquerait que ce panneau soit le seul à avoir été coupé sur les bords supérieur et inférieur.

Toutes ces observations jointes aux données de preuve nouvelles apportées par l'examen technologique approfondi du *Festin* et de la *Décollation* autorisent, pensons-nous, à conclure, comme le faisait déjà N. Reynaud, que ces panneaux proviennent du retable de *St-Jean-Baptiste*. Ce dernier serait le premier travail documenté de Juan de Flandres exécuté en Espagne. La *Naissance* et le *Baptême du Christ* appartiendraient plus que probablement au même ensemble, mais pour en détenir une preuve irréfutable, il faudrait aussi soumettre ces panneaux à une analyse dendrochronologique et à une étude plus poussée de la technique picturale. Déjà l'examen scientifique du panneau de Cleveland, publié en 1976 par Ross M. Merrill (17), montre les analogies de technique d'exécution que cette oeuvre partage avec le *Festin* et la *Décollation*. Nous ne possédons malheureusement pas de matériel de comparaison identique pour le *Baptême* (18).

Cette étude constitue un nouveau jalon dans "l'épopée" du retable de *St-Jean-Baptiste* permettant pour la *Décollation* et le *Festin d'Hérode* de passer de l'hypothèse à la certitude. Il reste néanmoins à compléter notre information sur la *Naissance* et le *Baptême* pour détenir toutes les données du problème et voir s'il s'agit d'un retable entièrement autographe de Juan de Flandres ou réalisé en collaboration avec Michel Sittow.

Enfin, le lien sus-mentionné—panneaux fabriqués avec des éléments provenant d'un même tronc de chêne de la Baltique—entre d'une part les panneaux de la *Décollation* et du *Festin* et de l'autre les deux panneaux (*Nativité* et *Piéta*) du retable de la *Vierge de Grenade-New-York* (19), copie du retable de la *Vierge* de Berlin dit retable *Miraflores* de Roger Van der Weyden, prouve que les supports de tous ces tableaux ont été construits à peu près au même moment et dans un même atelier travaillant pour Isabelle la Catholique, probablement l'atelier de Juan de Flandres, peut-être partagé avec Michel Sittow.

Il s'agit là d'une information inédite qui jette un jour nouveau sur l'auteur probable de la copie du retable de *Miraflores* de Berlin (20) qui fut l'objet de controverses passionnées jusqu'à la publication de R. Grosshans qui en établit définitivement le caractère autographe (21).

## Notes

1. Le suivi scientifique du projet a été assuré par C. Périer-D'Ieteren dans le cadre du Centre de Recherche et d'Etude technologique des arts plastiques de l'Université Libre de Bruxelles qui en est le promoteur. L'examen scientifique de la *Décollation* et du *Festin* a été rendu possible grâce à la compréhension de Messieurs Claude Lapaire et Hans Nieuwdorp, directeur du Musée d'Art et d'Histoire de Genève et conservateur des Musées d'Art et d'Histoire de la ville d'Anvers et de Madame Liliane Masschelein, directeur de l'Institut royal du Patrimoine artistique à Bruxelles. Nous les en remercions vivement.  
Anne Rinuy du laboratoire du Musée d'Art et d'Histoire de Genève et C. Périer-D'Ieteren se sont chargées de l'examen comparé de la technique picturale de la *Décollation* et du *Festin* s'aidant des réflectogrammes infrarouges et des radiographies exécutées, pour la *Décollation* par Anne Rinuy et Colette Hamard au Laboratoire du Musée d'Art et d'Histoire et pour le *Festin* par Guido van de Voorde de l'Institut royal du Patrimoine artistique (IRPA). L'étude stylistique et historique a été réalisée par C. Périer-D'Ieteren. L'examen dendrochronologique a été mené par Jozef Vynckier (IRPA) en collaboration avec Alain et Christian Orcel et Peter Klein (voir note 5), celui de la stratigraphie picturale par Anne Rinuy et Thérèse Flury, et par Léopold

- Kockaert (IRPA). La synthèse des résultats est présentée dans une même étude rédigée par C. Périer D'Ieteren avec la collaboration de tous les intervenants.
2. *Décollation*, chêne  $87 \times 47 \times 1$  cm, deux éléments A (29,4cm) et B (17,5cm).  
*Festin*, chêne  $76 \times 50,1 \times 1,1$  cm, trois éléments A (2,5-3,4 cm) B (31,4-31,8 cm) et C (16,3  $\times$  14,9 cm).
  3. Pour la *Décollation*, le côté gauche a été coupé, tandis que les bords droit et inférieur ont été rabottés sur la tranche. Pour le *Festin*, les bords supérieur et inférieur ont été coupés. Il est malaisé de prendre position pour les bords latéraux. La *Décollation* présente des traces de chevilles dans le haut du panneau à 0,7 et 4,7 cm du bord supérieur, le *Festin* des traces de clous à 2,4 cm du bord inférieur. S'agit-il de traces de traverses ou de fixation ultérieure dans un nouvel ensemble?
  4. Dans le *Festin*, les quatre bords ont été chanfreinés, et ce, après l'application de la peinture au revers et le raccourcissement des bords supérieur et inférieur. Ces parties moins denses apparaissent en foncé sur la radiographie. Une épaisse couche de cire, appliquée lors de la restauration par F. Bender en 1955 ou en 1966, recouvre le revers du panneau à l'exception des bords sur environ quatre centimètres.
  5. La *Décollation* a été datée par J. Vynckier à partir des mesures dendrochronologiques effectuées par A. et Chr. Orcel ainsi que Jean Tercier (LRD) à Moudon, Suisse; cette datation fut confirmée par P. Klein de l'Université de Hambourg, Allemagne.
  6. Ceci est le cas pour la plupart des peintures des anciens Pays-Bas. Le nombre de cernes d'aubier des chênes de la Baltique fluctue autour d'une médiane égale à 15 (min.9; max.36) tandis qu'en 50% des cas il varie entre 13 et 19; voir P. Klein, D. Eckstein, T. Wazny, J. Bauch, *New Findings for the dendrochronological dating of panel paintings of the 15th to 17th century*. ICOM Committee for Conservation, 8th Triennial Meeting, Sydney, Australia, 6-11 September 1987: Preprints, Los Angeles 1987, p. 51-54.
  7. Le troisième panneau de ce retable *L'Adieu du Christ à sa Mère* se trouve au Metropolitan Museum de New York et a été daté par dendrochronologie par P. Klein (date d'abbatage: 1474) qui confirme (lettre de décembre 1992) que les planches constitutives du panneau proviennent du même tronc de chêne que celles des panneaux de la *Nativité* et de la *Piéta* de Grenade.
  8. N'ayant pas eu l'occasion de voir les réflectogrammes, nous nous basons sur la description du dessin sous-jacent donné par Ishikawa (voir note 11).
  9. C. Périer-D'Ieteren, *Colyn de Coter et la technique picturale des peintres flamands du V<sup>X</sup> siècle*, Bruxelles, 1985, p. 39-40.
  10. Dans le *Festin*, la lecture de la radiographie est rendue confuse à hauteur de la robe de Salomé par l'image de la peinture du revers qui interfère avec celle de la face.
  11. Pour un état de la question des attributions jusqu'en 1976, voir Ann Tzeutschler Lurie, *Birth and Naming of St. John the Baptist attributed to Juan de Flandes. A Newly Discovered Panel from a Hypothetical Altarpiece*, dans *The Bulletin of the Cleveland Museum of Art*, 63, 1976, p.126-127. L'auteur avance l'hypothèse d'une collaboration entre Juan de Flandes et Michel Sittow dans l'exécution des panneaux du retable de *St-Jean-Baptiste* (p.132).  
C. Ishikawa, Le "*Retablo de la reina catolica*" by Juan de Flandes and Michel Sittow, Bryn Mawr College, 1989. Thèse de doctorat publiée en 1991 qui constitue l'étude la plus récente sur Juan de Flandes.
  12. N. Reynaud a brillamment démontré ce qui sépare les deux maîtres et nous adhérons pleinement au relevé des caractères stylistiques qui lui paraissent propres à Juan de Flandes. J. de Coe et N. Reynaud, *Origen del Retablo de San Juan Bautista atribuido a Juan de Flandes*, dans *Archivo Español de Arte*, 52, 1979, p. 133-144.
  13. Ann Tzeutschler Lurie, 1976, *op.cit.*
  14. J. de Coe et N. Reynaud, 1979, *op.cit.*
  15. *op.cit.*, 1979, note 13 donnant en cm. les mesures approximatives relevées alors: niche centrale:  $\pm 190 \times 110$  (Madrid:  $185 \times 109$ ), niches latérales:  $86 \times 47$  à  $52$  suivant la baguette de raccord (Cleveland et Genève:  $88 \times 50 \times 87 \times 47$ ), niche supérieur:  $\pm 75 \times 48$  (Anvers:  $76 \times 50,1$ ).
  16. J. de Coe et N. Reynaud, *op.cit.*, 1979. N. Reynaud n'accepte pas la reconstitution du tryptique original proposée par Lurie. Comme d'ordinaire les scènes latérales se suivent chronologiquement de haut en bas et de gauche à droite, elle placerait la *Décollation* après le *Baptême*, c'est-à-dire à droite au-dessus du *Festin*, situerait la *Naissance*, en bas à gauche, les deux compositions étant symétriques dans la construction du carrelage et du plafond, et suggérerait en haut à gauche, une *Visitation* comme scène manquante.
  17. Ross M. Merrill, *A Technical Study: Birth and Naming of St. John the Baptist*, dans *The Bulletin of the Cleveland Museum of Art*, vol. LXIII, 5, 1976, p.136-145.  
Nous n'avons malheureusement pas vu le tableau. Néanmoins sur base de l'examen des photographies, nous ne sommes pas convaincus de son attribution à Juan de Flandes. La composition nous paraît moins monumentale et plus chargée que celle



- du *Festin* et de la *Décollation*. Les personnages sont plus trapus et les drapés plus lourds. L'écriture picturale des détails nous semble aussi moins incisive (cheveux et barbe de Joachim, par exemple). Enfin, les photographies dans l'infrarouge ne laissent pas entrevoir de dessin de modelé hachuré. Les seules analogies de technique d'exécution pourraient s'expliquer par une même formation de deux artistes contemporains. L'attribution du *Baptême du Christ* à Juan de Flandes, déjà établie par la critique de style (I. Vandevivere, cat. *Juan de Flandes*, Louvain-la-Neuve, 1985, p. 50-53), nous paraît par contre pouvoir être acceptée. L'oeuvre a été examinée en réflectographie infrarouge par C. Ishikawa et C. Garrido qui en annoncent une prochaine publication.
18. Seuls trois échantillons ont été prélevés: un de préparation par L. Kockaert (IRPA) en 1985 lors de l'exposition *Juan de Flandes* à Louvain-la-Neuve; elle s'avère également être à base de gypse, l'autre dans le ciel, dont le bleu constitué d'azurite et de blanc de plomb liés avec un mélange huile-protéine, est semblable à celui de la fenêtre de droite dans le *Festin*. Le troisième échantillon, prélevé dans le manteau vert, semble constitué de deux couches: un glacis surmontant un mélange de vert et de blanc, ce dernier posé sur une couche (d'impression ?) grise.
  19. Cette découverte a été faite par J. Vynckier de l'IRPA qui a eu l'occasion la même année d'examiner le *Festin*, d'en comparer les résultats à ceux de la *Décollation* et d'analyser la *Nativité* et la *Piéta* du retable de Grenade-New-York.
  20. L'étude approfondie de la collection des peintures flamandes conservées à la Capilla Real de Grenade est en cours et fera l'objet d'une publication ultérieure. Cette étude s'inscrit dans le cadre d'un projet pilote coordonné depuis janvier 1991 par l'Institut andalou du Patrimoine historique (IAPH) de Séville, portant sur l'étude, la restauration et la présentation muséologique des biens mobiliers de la Capilla Real. C'est un travail de collaboration international auquel participent pour la Belgique l'Institut royal du Patrimoine artistique (IRPA) à Bruxelles chargé des examens de laboratoire et de la restauration et l'Université libre de Bruxelles (U.L.B.) qui mène l'étude d'histoire de l'art et l'investigation scientifique des peintures flamandes des XVe et XVIe siècles.
  21. Roger van Schoute, *La Chapelle royale de Grenade, (Les Primitifs flamands, I. Corpus de la peinture des anciens Pays-Bas méridionaux au XVe siècle, 6)*, 1963, p.87-109 et R. Grosshans, Roger van der Weyden. *Der Marienaltar aus der Kartause Miraflores*, dans *Jahrbuch der Berliner Museen*, XXIII, 1981, p.49-112.

### Crédit photographique

Fig. 1 Y.Siza, Musée d'Art et d'Histoire de Genève.

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Fig. 7a Y.Siza, Musée d'Art et d'Histoire, Genève.

Fig. 7b James Walker, Amparo Corporation, Santa Fe, NM.

Fig. 7c B. Jacot-Descombes, Musée d'Art et d'Histoire de Genève.

## Abstract

The examination and restoration of Gerard Dou's *The Young Mother* (1658) in the Mauritshuis is briefly described. A technical examination and analysis of paint samples was done using microscopy, elemental analysis by electron microprobe, and Fourier-transform infrared analysis (FTIR). Gas chromatography-mass spectrometry (GC-MS), carried out at the National Gallery in London, identified the original paint exhibiting broad cracks as bituminous. The typical pale blue areas contain finely ground ultramarine. The painting technique is compared to other 17th century Dutch painters.

## Keywords

Gerard Dou, ultramarine, asphaltum, bitumen, craquelure, Fourier-transform infrared analysis (FTIR), Gas chromatography-mass spectrometry (GC-MS)



Fig. 1: G. Dou, *The Young Mother*, Mauritshuis, The Hague, inv. nr 32, after restoration.

## The Restoration and Technical Examination of Gerard Dou's *The Young Mother* in the Mauritshuis

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## Introduction

Gerard Dou's *The Young Mother* (See fig. 1) (The Mauritshuis in The Hague, inv. nr 32) is painted on an oak panel consisting of one radially cut plank 73.5 cm high and 55.5 cm wide with a thickness of 5–6 mm. It has an arched top. The picture retains its original format. It is only slightly beveled at the top and has no cradle. The inscription GDOV 1658 is painted in the leaded window (1).

The Staten van Holland and West-Friesland bought the picture from Dou's own studio as part of a diplomatic gift for Charles II, the new King of England. In 1660 the "Dutch Gift" was shipped to England. The Dutch Stadhouder William III, who had become King of England in 1688, brought the picture back to Holland to his palace 't Loo. In 1763, after moving to a few other locations in The Netherlands, the picture's home became The Hague (2). Its stay was interrupted by twenty years in France during the Napoleonic era as loot of war, together with about two hundred other paintings of the Stadhouder's collection (3). Since 1821 it has belonged to the Royal Cabinet of Paintings Mauritshuis Collection.

In 1986 the picture came to the restoration studio of the Mauritshuis because of severe blistering of the paint. Blisters were present in several areas, oriented perpendicular to the wood grain. As a result of an earlier varnish application while the picture was in this blistered state, the varnish layer appeared "closed". In spite of this, it was possible to stick the blisters back in place using a low molecular polyvinyl alcohol glue (Mowiol 4-88) at ca 40°C.

Blister-laying with the water-based glue resulted in some crazing of the varnish layer. Also, there were badly discoloured retouches. Some of the retouches were not only discoloured but had a disfiguring effect on the picture because of their shape and consistency. Some areas, for instance the drapery hanging from the balustrade, were totally overpainted. The reason for the complete overpainting could be learned from the X-radiograph; the overpainted original showed broad drying cracks. The esthetic disturbance due to the cracks was an additional stimulant to clean the picture.

## History of restoration

The documentation on treatments of the picture retrieved goes back to its return from France. It exists as short notes without elucidative illustrations.

In 1815, cracks (most likely the ones visible in the background now) were referred to with the recommendation of filling and retouching them. This was executed in 1816 when the picture was cleaned. Later in the 19th century the painting was revarnished, and the varnish was "repaired" at least six times, as in 1887, when in the same letter, although concerning other pictures, copaiva balsem is mentioned as "a totally harmless means" for softening paint. In 1898

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the varnish was regenerated, and in 1907 the painting was again restored. It was then immediately framed behind glass because "the painting is very often examined [sic] at a short distance and even with the aid of magnifying glasses" (4). In 1922 it was cleaned again, retouches were adjusted and the painting was varnished. There was another restoration in 1954, and sometime before 1970 the picture was varnished in its blistered state. No mention is made of blistering in earlier reports.

Although the filling of cracks is mentioned only once in earlier reports, three different types of filling were found during the 1986/7 restoration. Therefore, when retouching was mentioned in early reports, it probably referred to (re)filling as well.

### **Treatment and restoration**

When the overpaint was removed, heavily puttied, wide alligatoring cracks, indeed became visible. The putty had been applied so as to level out the whimsical river landscape formed by the cracks, in order to match the other intact and smooth areas of the painting. The putty not only covered the cracks, but also the inward sloping original topmost paint along the cracks, making the cracks appear even broader than they actually were.

In the narrow center of some of these cracks there was a dark brown material that must have surfaced from the underlying areas in a fluid state at some stage. After the overpaint had been removed from the window curtain, it was apparent that the original paint of the curtain was very damaged. The three different types of filling were found in this area. In other areas, for instance the dark brown top part of the picture (including the balustrade), the paint layers were also worn and bitten away, exposing a lumpy surface.

We are usually tempted to accept this type of drying craquelure and make no attempt to hide it. This craquelure often occurs in 18th and 19th century paintings as a feature of a particular use of painting materials. Apart from the ethical reason for this, there is the possibility of discolouration of new retouches, which subsequently might have to be removed again someday. For instance, the badly discoloured retouches that were removed in 1986/7 were only 32 years old.

However, as Dou was the best representative of the *fijnschilders* (fine-painters) and was often admired for his illusionistic painting, the disturbing cracks contrasted with the image we have of Dou. His way of achieving the illusion was by painting in a very detailed and smooth manner with no visible brushstrokes. Already in 1660, shortly after the picture had arrived in England, the art critic John Evelyn, who saw the picture in the Palace, admiringly wrote that the piece "(was) painted . . . so finely as hardly to be at all distinguished from Enamail" (6).

Although the pronounced cracks we see now are mostly situated in areas away from the main scene of the picture, they were found to be too disturbing and attracted too much attention. Dou's perfectionistic painting technique caused us to take retouching quite a few steps further than usual. Not only the wide cracks, even many of the small crow's foot cracks were inpainted. Worn, thin, white glazes and scumbles were retouched as well. Contrary to the earlier restoration, the slopes of the wide alligatoring craquelure were not filled, leaving the misformed relief of the original paint visible.

### **Scientific examination**

#### *Method*

The picture was examined in 1986. Photographs were made using normal, raking, and ultraviolet light. X-radiographs were made of the whole picture, and infrared reflectographies were made of the bottom portion. The painting was examined under the stereomicroscope to further assess its condition and build-up, and to remove paint samples.

The numerous losses in the paint film made the removal of tiny samples possible in this miniature-like picture. The samples were made into cross sections by embedding them in a polyester resin and grinding and polishing the blocks until the sample was exposed on the surface of the block. The cross sections were studied in dark-field reflected light, polarized reflected light, and ultraviolet fluorescence. Blue pigment particles were mounted in Canada balsam for examination in transmitted light and with crossed polars. Microchemical tests were done in a few cases. Elemental analysis was done systematically using an electron microprobe with an energy dispersive X-ray analyser (SEM-EDS) at the Department of Earth Science, Cambridge. Raymond White of the Scientific Department, National Gallery, London, used gas chromatography-mass spectrometry (GC-MS) for the identification of the brown paint exhibiting alligatoring cracks. In addition, Fourier-transform infrared analysis (FTIR) was used for its identification at DSM-Research. Gas chromatography was used on one of the samples for the identification of the medium.

#### *Changes in the composition*

The coat of arms in the leaded window indicates the possible commissioner of the painting, who died a year after his marriage in 1652; only three months later, in 1654, the son died as well. Broos speculates that under these circumstances withdrawal of the commission could have occurred and that the picture would have stayed in Dou's studio for about seven years. Dou would have "freshened-up" the picture to make it suitable for the delegation that came to his studio in 1660 (7).

The stereomicroscope revealed that the date contains two layers of paint, one more blackish, one more brownish, which could indicate that Dou changed the date from 1653 (or 1652) to 1658. We could not confirm this in our examination and no sample could be taken for further examination. However, even if Dou did finish the picture in 1658 (the date shown on it) this would have given him plenty of time to reconsider the composition. Such events would explain the unexpected number of *pentimenti* and the possible change of date. To name just one, and the most spectacular of the changes: the face of the girl behind the cradle was originally turned to the left, towards the mother. This can be seen with the naked eye through the worn, translucent paint. Her proper right eye even shows through the more opaque white of her headdress. The headdress original face is of a very young child.

#### *The structure and composition of the paint layers and ground*

##### *Ground*

When examining the damaged left-hand side of the picture under the stereomicroscope, there appeared to be a chalk ground with a thin ochre-coloured *imprimatura*. The cross sections demonstrated that the application of chalk was very thin; it is really only a little glue (now discoloured brown) with a little chalk and black pigment added to it. Because of its thinness it is absent in some of the samples. The application of the ground in different areas does not seem to be consistent. It is very difficult to decide from the cross section which layer belongs to an overall ground and which does not. Judging from the vague image on the X-ray, the ground seems to have been applied in long, straight strokes. On the damaged left-hand side of the picture a few small paint samples could be removed. Even in this small area there are differences: in one spot there is a 10  $\mu\text{m}$  thin whitish ground of lead white and chalk, in another spot a thin brown layer of red ochre and possibly bone black. Underneath the dark shadow on the floor in the foreground there is a much thicker chalk ground and there is a thin one under the chandelier, where a little lead white and umber are mixed through the chalk (8).

##### *Underdrawing*

Infrared reflectography (See fig. 2) showed clear lines, indicating the use of a carbon black, most obviously visible in the sketch of folds in the mother's skirt. Less strong lines could be seen in the platform that was originally planned on



Fig. 2: Infrared reflectography of the left bottom corner, done by E. Klusman of the Central Laboratory in Amsterdam.



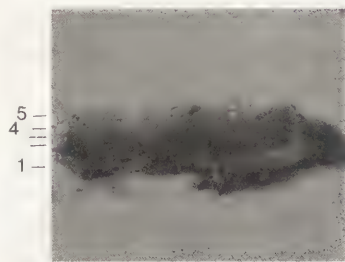


Fig. 3: Sample 1, blue in the cradle. Fine ultramarine in layer 5. Layer 4 is lead white. Layers 1–3 are underlying brownish paint.

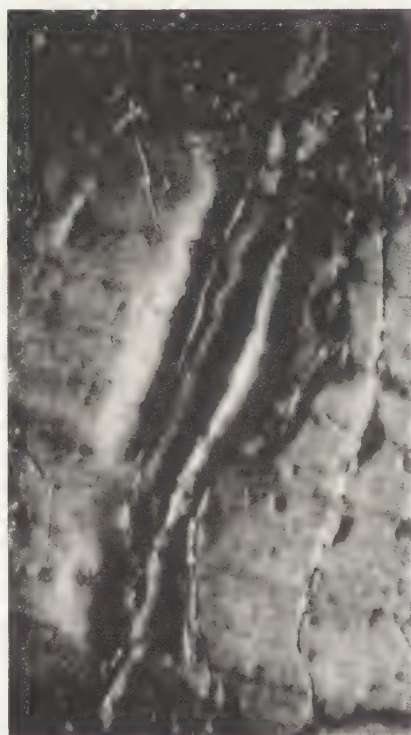


Fig. 4: Alligatoring cracks in the drapery hanging from the balustrade worsened by reforming.



Fig. 5: Cracks in the girl's face with dark material protruding from underlying layers.

the floor. Here the lines are weaker but very uniform and straight, seemingly drawn in pencil along a ruler.

#### Paint layers

The ashen blue areas, such as the mother's skirt, the blanket, and other draperies in the cradle, give the impression of having faded and become thinner in the course of time (9). In the mother's skirt, the blue sits in rows of tiny droplets or dots of paint on a whitish underlayer, imitating the effect of a pattern in a translucent blue cloth. The dots are very fine and run in rather regular waving lines unrelated to the folds of the skirt. At first we assumed that Dou made the pattern by mechanical means, for instance a comb, a fine screen, or the ball of the thumb. Since we failed to imitate the effect by such means, we dismissed the hypothesis. Our conclusion now is that Dou, in his attempts at perfectionism in "finepainting", may have painstakingly painted them dot by dot (10). The dots are indeed somewhat irregular in size, measuring ca 1 mm. The ca 2–3  $\mu\text{m}$  blue particles were identified as ultramarine. (See fig. 3)

Tiny yellowish droplets appear on the paint of the window on the left. The black paint used for the leaded window shows drying cracks which make the black paint appear as drops as well. Glazes pulled together into droplets are present in several other places, for instance in the cradle and in the foreground. There seem to be problems due to surface tension and insufficient wetting.

Examination with the stereomicroscope along the broken edge on the left-hand side exposes a wavy pattern in several thin, superimposed paint layers. The wavy pattern could indicate that a paint layer was not dry when the next one was applied. The embedded sample shows at least four thin paint layers in the cross section, ranging from grey to light yellowish, on top of the ground underneath the paint layer of the blue sky. The blue sky itself was painted with two superimposed layers, ca 12  $\mu\text{m}$  each, of lead white and very finely ground (ca 3  $\mu\text{m}$ ) ultramarine. There are also very thin (ca 2  $\mu\text{m}$ ) intermediate layers of medium. A thin brown pigmented layer runs into a crack in what is presumably the ground, indicating that the ground was already dry when subsequent layers were applied. The total thickness of the paint used for the window measures, surprisingly, up to ca 120  $\mu\text{m}$ .

Numerous thin, superimposed layers were found in other places as well. In the shadow on the floor, beneath the leg of the chair in the lower left, brown paint layers with a total thickness of ca 90  $\mu\text{m}$  were found. Elemental analysis showed that umber is a main ingredient in these brown layers, with lead white and chalk mixed in. Again there is a wavy pattern.

#### Dark paint exhibiting dry cracks

The picture displays coarse alligatoring cracks in the drapery hanging from the balustrade (See fig. 4), the lamp hanging from the ceiling, the window curtain and the brown background. A finer crow's foot crack pattern can be seen in the girl's face (See fig. 5) and on some of the dark-coloured objects in the light-coloured foreground (See fig. 6). In the girl's face, where the cracks were never retouched, the stereomicroscope revealed that the cracks appear so dark because brown material from underlying layers protrudes through the cracks. The likely cause of this is provided in reports from the turn of the century that mention the use of copaiva balsam and regeneration. We presume that attempts at improving the appearance of the alligatoring or the varnish failed and instead have worsened the cracks in the paint layer (12). There is wrinkling of dark paint layers in the background above the window. The wrinkling, alligatoring and crow's foot cracks are clear signs of problems with the drying of the paint (11).

To the right of the lantern in the foreground on the right, five thin brownish and greyish paint layers are superimposed. In between these, there are thin applications of medium that strongly fluoresce in ultraviolet light under the microscope; these areas have not yet been analysed.

The thin, intermediate layers of medium and some areas on top of the paint (for instance in the window and in the foreground) could be responsible for the



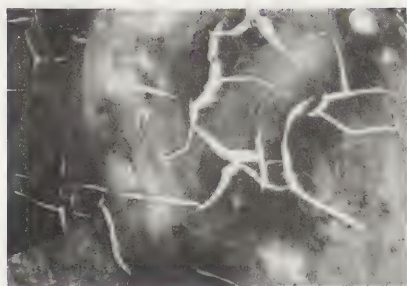


Fig. 6: Crow's foot cracks in the earthenware pot on the floor.

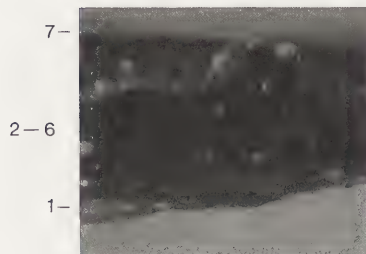


Fig. 7: Sample 2, the chandelier. Layer 7 is the light-coloured chandelier. Layers 2-6 are underlying layers of brown and black paint. Layer 1 is the lead white and chalk ground.

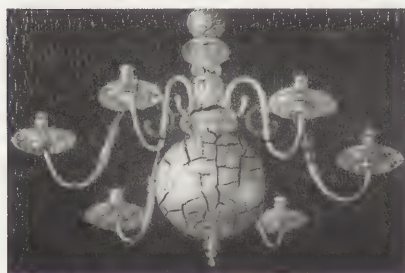


Fig. 8: Alligatoring cracks in the chandelier where sample 2 (Fig. 7) was taken, after cleaning.

strange droplets that sit on the surface. The black paint in the window gives the impression of Bernard cell formation, and the droplets in the foreground are indicative of problems with wetting and surface tension.

A multiple layer structure is present in the alligatoring dark background as well. A tiny sample (See fig. 7) from the chandelier, where the cracks are very obvious in the light- coloured paint (See fig. 8) of the lamp, shows at least twelve layers of alternating brown and black paint with a total thickness of ca 145  $\mu\text{m}$  underneath the thin (ca 7  $\mu\text{m}$ ) yellow paint layer of the lamp. The cross section shows a black layer pushing itself upwards through the top paint. As a result, the quick-drying yellow paint (lead white, yellow ochre, umber) is no longer a continuous film. It is surprising to find the cracks not only on the scale of the alligatoring, but also on this microscopic scale.

Although it is not very obvious when the cross sections are examined under the light microscope, elemental analysis and FTIR spectra show that there is a high proportion of chalk present in the dark underlayers. Besides chalk, there is umber, red ochre, bone black, and a little lead white in brown layers that belong to the architecture. Chalk, bone black with less ochre, and lead white are present in the thick, blackish layer that protrudes upwards. Coarse, alligatoring cracks are often associated with the use of asphaltum or bitumen. It was mentioned for use as a pigment by Borghini in 1583, as Nero di Spalto, and recommended by De Mayerne in the 17th century for glazing and shading (13). It is not possible to recognize bitumen or asphaltum in the cross section, because this pigment dissolves in the oil medium. It is already dissolved in the preparation of the paint, because the pigment is not ground and mixed with the oil, but instead is pulverized and dissolved in a drying oil with litharge when heated. With the techniques of gas chromatography (GC) and GC-MS, linseed oil and hopane-like triterpenes could be identified, which indicate the presence of asphaltic or bituminous material in the oil medium (14). The group of bands between ca 700 and 900  $\text{cm}^{-1}$ , characteristic of bituminous materials, could not clearly be distinguished in the tiny, complex sample of aged paint.

### Conclusions

In the 17th century Dou's painting technique was compared to enamel. Also Sandrart's account, after visiting Dou in his studio, is a testimony of Dou's precise manner of working:

"... he rubs down his colours on glass, and makes his brushes himself; he keeps his palette, brushes and paints carefully put away out of the dust which might soil them, and when he prepares to paint he will wait quite a long time till all dust has completely settled. Only then does he very quietly take his palette out of its box near at hand, the prepared colours and brushes, and begins to work; and when he has done he puts everything carefully away again" (15).

Sandrart also noted that Dou painted with the aid of eyeglasses (16). The very finely ground pigments, the thin, superimposed layers of paint and, for instance, the meticulously painted skirt of the mother seem in agreement with these descriptions. However, certain aspects of the painting technique in *The Young Mother* seem to contradict them. These aspects include the droplets in and on the paint film, indicating problems with wetting, the coarse alligatoring and finer crow's foot cracks, due to slow drying of the dark paint containing asphaltum, the wrinkling of the paint film (again, indicative of problems with drying), and the use of fast-drying, thin opaque paint layers. (For instance, the flesh of the girl's face and the chandelier, and thick ones such as in the red drapery, were painted on top of thick dark paint that was not thoroughly dry.)

The reason for the choice of a pigment with poor drying properties, asphaltum, must have been its recommendation for shading and glazing. But instead of using asphaltum for this purpose, he used it in underlayers notwithstanding the warnings. How soon the drying cracks would have appeared and whether Dou was able to see them on his pictures is a matter for further study.

In his use of numerous, very thin, superimposed layers with very finely ground



pigments, Dou differs from other 17th century painters, such as Frans Hals and his teacher in his early years, Rembrandt.

### Notes

1. The spot chosen for the inscription is interesting. Dou, *Leiden 1613–1675 Leiden*, was the son of a glass maker and trained as a glass engraver before he became apprenticed to Rembrandt in Leiden in 1628.
2. Ben Broos, *Meesterwerken in het Mauritshuis* (The Hague: Staatsuitgeverij, 1987), 111–119.
3. Ghislain Kieft, "Ordentelijk en planmatig. De grootste kunstroof uit de geschiedenis," *Kunstschrift* 2, (1991): 18–38.
4. Annual report of the Mauritshuis, 1907.
5. Luuk M. Struick van der Loeff, "Problemen, overwegingen en beslissingen bij de conservering en restauratie van het schilderij door Gerard Dou 'Jonge moeder', 1658, Mauritshuis inv. nr 32", *CL Themadag* 12, (1987): 40–51, 69–71. (In Dutch, with English summary 75–6).
6. E.S. de Beer, *The Diary of John Evelyn* (London 1959), 413.
7. Broos, *Meesterwerken*, 117.
8. Dou's *Der Junge Gelehrte* in the Herzog Anton Ulrich-Museum, inv. nr 234, has a less complicated ground structure. The white ground was identified by the Doerner Institute, Munich, as a mixture of chalk and lead white with a glue medium.
9. A.M. de Wild, *The Scientific Examination of Pictures* (London: G. Bell & Sons Ltd., 1929). De Wild chose *The Young Mother* as an example of the occurrence of "ultramarine sickness" when trying to unravel the cause of the greyish-blue effect. He identified the blue as ultramarine and found that (most of) the pigment had retained its colour.
10. A similar pattern can be found in the upper part of the curtain on Dou's *Maid Servant at the Window*, Museum Boymans van Beuningen, Foundation Willem van der Vorm nr 21 and in non-related earlier paintings from Brussels around the end of the 15th century with hand-painted dots on the gilded background.
11. Alligatoring crack patterns appear in many other pictures by Dou, although not in all. So far, we could detect them in a light form in pictures from 1636 onwards, and in a coarse form from 1653 until 1671.
12. Sibylle Schmitt, "Das Pettenkofersche Regenerationsverfahren" *Zeitschrift für Kunsttechnologie und Konservierung*, (4/1990): 30–77.
13. Il Riposo di Raffaello Borghini. All' illustriss. et Eccellentiss. sig. Pardron suo singulariss. il Sig. Don Giovanni Medici. (Florence: 1583), 208.  
J.A. van de Graaf, *Het De Mayerne Manuscript als Bron voor de Schildertechniek van de Barok* (Mijdrecht: Ph.D. diss., Utrecht University, 1958), 178.
14. We are grateful to Raymond White for doing the analysis. Report Scientific Department, National Gallery, London. The A/P ratio of 100/53.60 = 1.87. The P/S ratio of 53.60/35.76 = 1.50 suggests the use of linseed oil. A ratio of 28.6/6.57 = 4.3 for the C9/C10 dicarboxylics shows that a heat-bodied oil has not been used. The presence of dehydroabietic and 7-oxodehydroabietic esters, together with the absence of larixol, norabietatrienes and retene-like components suggests the inclusion of pine resin, but no evidence for larch resin, softwood pitch or resin tars. No triterpenoid components of the dammar/mastic types were detected. A mass scan for hopane-like triterpenes identified an homologous series. Asphalt was identified by R. White in black paint of a picture by Van Dijck as well.  
(R. White, "Brown and Black Organic Glazes, Pigments and Paints", *National Gallery Technical Bulletin* 10, (1986): 58–72.) The hopane-like structures derive from bacteria involved in the geological modification of organic matter. They are referred to as chemical fossils and act as biological markers in the sedimentary organic matter that gives rise to asphaltum and bitumen.
15. W. Martin, *Het Leven en de werken van Gerrit Dou* (The life and the work of Gerrit Dou), Leiden 1901, translated in English: *Gerard Dou* (London: Editor G. Bell & Sons, 1902), 85.
16. A.R. Peltzer, *Joachim von Sandrarts Academie der Bau-und Mahlerey-Künste von 1675* (Munich, 1925), 195.

### Abstract

Very few 14th-century Italian paintings on canvas are known and so far no technical examination of the materials and techniques has been reported. The paper describes four late 14th-century paintings and compares the technique with the account given in Cennino Cennini's *Il Libro dell' Arte*. The contrast between this technique and that found in Northern Europe in the 15th century is noted.

### Keywords

Painting technique, Italian, paintings support, Cennino Cennini, linen, egg tempera

## The Technique of Four 14th-Century Italian Paintings on Fabric Supports

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### Introduction

At present, four early Italian paintings on fabric supports are undergoing treatment in the Conservation Department of the Courtauld Institute of Art, London. The paintings represent narrative scenes from the Passion of Christ: *The Washing of the Disciples' Feet*, *The Betrayal of Christ*, *The Flagellation*, and *The Mocking of Christ* (See figs. 1, 2). The original location of the paintings is unknown. The paintings were in the collection of William Young Ottley (1771–1836) and passed through his family in 1849 to the Church of St. Michael and All Angels, Withyham, Sussex, where they have remained until the present day, excluding a brief period at the end of the 19th century. William Young Ottley spent time in Italy from 1791–99. Here, he studied and purchased works of art and it is assumed that these works were acquired at that time. On the grounds of style, the paintings are thought to be Florentine from the last quarter of the 14th century, possibly from the circle of Niccolo di Pietro Gerini.



Figure 1. The Flagellation, Church of St. Michael & All Angels, Withyham, Sussex.

The use of fabric as a support for painting in the 14th century is well documented although very few examples survive. The Withyham paintings are unique in depicting four scenes in a continuous narrative. Other surviving paintings on fabric supports and the historical context of the Withyham paintings are dealt

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with in another paper (1). In general type, the closest comparison that can be made is with four scenes executed circa 1336 by the Master of the Franciscan Temperas, a Neapolitan artist working for Robert of Anjou, King of Naples. These paintings, which are similar in size and format, show the Madonna and Child, St. Francis receiving the Stigmata, the Flagellation of Christ, and the Crucifixion (2).

The two most important sources for painting techniques around 1400 are Cennino Cennini's *Il Libro 'dell Arte* and Jean Le Beque's compilation of manuscripts copied in Paris in 1411 (3, 4). Both give clear instructions for painting and gilding on fabric. The passages in the Le Beque compilation, principally Alcherius' *De Coloribus Diversis Modis Tractatur* correspond more closely with Northern European practise. Cennini describes painting funeral palls, wall hangings, clothing, and most importantly, banners. Where the technique for painting a banner differs from a panel painting, his description is quite full, so the application of the ground and gilding are dealt with in considerable detail; of painting forms, he says only that the painter should proceed "in the same way as for anconas . . . step-by-step." The technique of the Withyham paintings bears close comparison with Cennini's account.



Figure 2. The Mocking of Christ, Church of St. Michael & All Angels, Withyham, Sussex.

### Fabric support

The four Withyham paintings all measure approximately 1 m<sup>2</sup> including decorative chevron borders. It is impossible to estimate how much has been lost from the borders since no original edge is present (5). Each consists of two pieces of fabric carefully seamed together using a neat backstitch. The seam is very pronounced on the back and excludes all possibility that the fabric could ever have formed a part of a normal panel painting construction, as has been suggested. All four paintings are executed on a medium-weight, closely woven linen fabric with an average weave count of 17 × 15 yarns per cm<sup>2</sup> (6). The individual yarns are rather varied and irregular, but the fabric is identical on all four paintings.

When the paintings came to the department, they were adhered with an animal skin glue to mahogany panels from which they had begun to delaminate. It is assumed that the paintings were mounted this way in England. We know very little about the way paintings on fabric supports were stretched originally. Cennini gave the following instructions for mounting: "Stretch it taut on a frame and begin by nailing down the lines of the seams and then go around and around with tacks to get it stretched out evenly and systematically" (7). The method of stretching would result in some cusping of the weave and a slight cusping is evident on the Withyham paintings, but not on all edges and not with as much distortion of the weave as one might expect.

Northern European practice was to use strings to lace the painting to the stretcher; this practice continued into the 17th century. This method is used to stretch animal skins for the preparation of parchment and also by embroiderers to hold their fabric, because it allows for easy re-tensioning. So far there is no evidence that this method was used in Italy at this time. It is also clear that sometimes the fabric was not stretched on a strainer but glued to a wooden panel and then a frame applied, nailed through painting and strainer at once. There is some evidence of this practice in the 15th century in Mantegna's paintings on fabric supports (8). However, it is argued that 14th-century Italian paintings were executed on fabric supports because they were intended to be portable and such a method of presentation would hardly be compatible with this function.

### Ground

In all the Withyham paintings, the ground layer is unpigmented white calcium sulphate and solubility tests indicate that the normal animal skin glue binding medium has been used (9). X-ray diffraction analysis of the calcium sulphate revealed a mixture of anhydrite ( $\text{CaSO}_4$ ) and gypsum ( $\text{CaSO}_4 \cdot 2\text{H}_2\text{O}$ ) rather than pure gesso sottile prepared by slaking burnt gypsum (10). There is no evidence of a layered application. In cross section, the ground looks very yellow, the result of staining by the glue used to adhere the linen to the mahogany panel. It is not possible to distinguish an original size layer on the fabric. Cennini gives the following instructions:

Take gesso sottile and a little starch or sugar and grind these things with the kind of size with which you tempered the gesso on panel; grinding them good and fine. . . . Take a knife blade which is even on the edge and straight as a ruler and lay some of this gesso on the canvas with this edge, putting it on and taking it off evenly as if you were scraping it down. And the less gesso you leave on the better just so you fill up the interstices between the threads. It will be amply sufficient to put on one coat of gesso . . . You may roll up and fold the cloth without hurting the gold and the colours (12).

No attempt was made to identify the presence of starch or sugar, but the addition of a humectant to reduce brittleness is notable. Cennini also recommends using weak size for the same reason.

Although only a thin ground layer is used, it has important implications for the painting technique and subsequent varnishing. Cennini also describes how to paint large-scale items such as wall hangings in "washes of colour" in cases where a ground layer would have been impractical (12). Northern European paintings on canvas supports typically do not employ a ground layer, instead relying entirely on the glue size application to prepare the fabric. The visual consequences of impregnating these paintings with either lining adhesive or varnish or both are well known (13).

As far as the authors can tell, a ground layer is present in all the early Italian paintings on fabric supports that they have seen and this has been confirmed by technical examination in the case of the Spinello Aretino banner (Metropolitan Museum of Art, New York) and the Barnaba da Siena banner (Victoria and Albert Museum, London), both of which are double-sided, the *Intercession of Christ and the Virgin* (Cloisters, New York), and Lippo di Dalmasio *Madonna of Humility* (National Gallery, London) (14).



### Underdrawing

The compositions are crowded and complex; forms do not overlap one another and the need for careful planning is obvious. Some underdrawing is visible to the naked eye and a limited amount can be detected using infrared photography and reflectography. The drawing is very simple: swift sweeping lines describing form and major drapery folds with little hatching or shading. The lines are soft fluid and of variable width, suggesting the use of a brush rather than a quill pen. In many cases, it is likely that the drawing cannot be distinguished from the strong outlining that is such a notable characteristic of the paint layer.

### Gilding

There are limited areas of gilding in the Withyham paintings. Gold leaf is employed as the equivalent of sky glimpsed through windows or beyond trees and silver leaf for the soldiers' armour. Mordant gilding is also widely used.

Cennini gives detailed instructions for gilding on fabric supports. He states that his method of water gilding is "a source of wonder among others" and seems to imply that oil gilding might be more commonly used. He describes using an underlayer for the gold. The underlayer is composed of calcium sulphate and Armenian bole bound with egg white and size. In the Withyham paintings, the gilded areas are damaged and overpainted. In cross section, there is a layer of red bole visible, but it is very thin and it is impossible to distinguish any admixtures. The technique appears to be water gilding. Cennini also gives instructions for burnishing and decorating the gold: "Lay your gold just as you do on panel and burnish it holding a very smooth and solid board underneath this cloth, keeping a cushion between the cloth and the board. And in this way, stamp and punch these diadems and they will be just the same as on panel" (15).

"Just the same as on panel" is a recurrent theme in Cennini's description. The double-sided banners by Barnaba de Siena and Spinello Aretino have gilded backgrounds, but often paintings on fabric supports have only blue backgrounds, presumably because of the expense. However, elaborate decorative effects are still employed; Simone de Crocefissi's *St. Helen Adoring the Cross* (Pinacoteca Nazionale, Bologna) has an azurite blue background but incorporates moulded elements in St. Helen's crown and diamond-shape appliqued features in the border. *The Intercession of Christ and the Virgin* (Cloisters, New York) also has a blue background, but the haloes are water gilded and painted with a pattern of crimson glazes and opaque white dots (16).

Mordant gilding is very commonly found in paintings on fabric supports. In the Withyham paintings, the mordant appears to be oil, pigmented with ochre and minium, which would also act as a dryer (17). The mordant is, consequently, strongly coloured.

It is in the context of discussing gilding that Cennini mentions varnishing banners to protect them: "You must varnish them afterward because sometimes these banners, which are made for churches, get carried outdoors in the rain; and, therefore, you must take care to get a good clear varnish and when you varnish these paintings, varnish these diadems and gold grounds a little, too" (18).

Water gilding might be expected to be the first area to suffer in rain, so the instructions are sensible. They may also be read to imply that on normal panel paintings, the gold was not varnished as were the painted areas (19).

### Paint layer

The paint medium has been identified as egg tempera, which is consistent with Cennini's directions "as for anconas" (20). The paint surface has all the characteristic features of egg tempera paint. Although the brushstrokes are somewhat broader and more evident than usual, they are applied and blended in such a way as to give all the forms a smooth, continuously modelled appearance. In general, the structure of the paint layers is fairly simple; it consists of one layer

in which a glazing effect is used; occasionally two layers of paint are used. Cennini advises laying in colours more thickly on canvas paintings than on panel "because the cloth has no body as the ancona has and it does not show up well under the varnishing when it is poorly laid in" (21). This is not borne out by the cross sections from the Withyham paintings.

Pigments have been identified using optical microscopy and, in some cases, scanning electron microscopy and energy dispersive X-ray microanalysis (22). So far, the following pigments have been found: ultramarine, azurite, artificial copper carbonate, vermilion, red lake, red iron oxide, minium (in the mordant), lead tin yellow, yellow lake, yellow ochre, green earth, charcoal black, and lead white. Ultramarine blue is quite widely used; mixed with lead white, it is generally painted in one layer without any grey, white, or even blue underlayer. The large, intensely coloured particles indicate that a good quality and, therefore, expensive pigment grade was used, however, some colourless siliceous particles are also mixed into the ultramarine in sufficient quantity to suggest an intentional adulterant or extender (23). Ultramarine is also found mixed with lead tin yellow for a bright green in drapery and mixed with red lake in the mauve shadow of Christ's white robe in *The Mocking of Christ*. The other blue pigment, azurite, is used in a similar way; it is used alone with lead white or mixed with lead tin yellow and yellow lake for a more acid green colour. This combination is described by Cennini, whereas he recommends orpiment to mix with ultramarine (24).

Azurite and ultramarine are both found in Christ's robe in *The Mocking of Christ*. As Cennini suggests and as a number of recent technical analyses have confirmed, ultramarine and red lake are mixed together in the violet shadows of the robe (25). Some fading of the red lake has occurred, as can be seen by comparing samples from below the mordant gilding with those exposed to light. A delicate pattern of red designs, blue stars, and mordant gilding was applied on top of the tinted white. The blue pigment in the stars is azurite; the paint is textured and medium rich, but the medium has not been identified yet.

Intensely saturated reds and purples are a striking feature of the paintings; interestingly these are achieved both by using red glazes over ultramarine and direct mixtures of red lake and ultramarine. Another rich purpleish hue is a mixture of red lake and red iron oxide. Red glazes are also found, generally badly deteriorated, over vermilion, as well as being applied directly over the ground. The variety of colours in the red lake pigments suggests that more than one dyestuff may be being used. A passage of yellow drapery seems to typify the painters search for varied colour effects: the bulk of the robe is lead tin yellow, but admixtures of vermilion and glazes of yellow lake are used to vary the hue and saturation.

In general, the use of colour in the Withyham paintings may be described as bright, decorative, and varied. This is seen, for example, in the exploitation of "cangiante" effects (yellow-green, yellow-blue, yellow-violet, yellow-red, and red-blue). The use of red and yellow lake pigments for glazing effects is notable and bears some comparison with the San Pier Maggiore Altarpiece by Jacopo di Cione' although, in general, the colours in the Withyham paintings are much more saturated (26).

The flesh modelling is unusually dark and warm in colour. This is explained by cross sections which show three layers of flesh modelling: a very thin layer of green earth directly on the ground; a "verdaccio" under modelling, incorporating vermilion as well as the usual black, and ochre; and a final layer of vermilion and lead white. In addition, many of the features and contours are strongly outlined. Interestingly, this strong outlining is also a feature of the Spinello Aretino banner and *The Intercession of Christ and the Virgin* (27).

### Varnishing

While no direct evidence survives, every aspect of the technique described by Cennini appears to take a final varnish into account. The type of oil resin varnish used in the 14th century would have been viscous and glossy. In this context,



it is interesting to speculate on the degree of difference in final surface appearance between these paintings on fabric supports and panel paintings.

### Conclusion

The technique of painting described so far bears comparison with Cennini's account for painting banners and may form a starting point for additional comparative work that has not yet been fully considered. The principle differences between the technique of the Withyham paintings and Cennini's account lie in the nature of the calcium sulphate used for the ground and the simplicity of the paint layers. The contrast is very striking between this technique and Northern European paintings executed in an aqueous medium on sized linen, especially if we take into account that Northern paintings were not varnished.

At present, work is continuing on the Withyham paintings. Only *The Flagellation* and *The Mocking of Christ* have been examined closely; it may be expected that as conservation work proceeds, more information on materials and technique will be gathered.

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# Working Group 2

Structural Restoration of Paintings on  
Canvas

Restauration structurale des peintures sur  
toile





## Abstract

The interruption of uniform stress by the presence of tears in canvas paintings is analyzed. Stress propagation and stress concentration are discussed. A proven way to treat tears is described involving the use of manipulation, moisture, heat, and pressure. Epoxy adhesives are recommended to provide the strength and stiffness required to prevent future deformation. Reference is made to use of the Mitka mini-suction apparatus. Lining is highly recommended after tear repair.

## Keywords

Canvas paintings, tears, stress propagation, treatment of tears, epoxy resin adhesive, Mitka suction apparatus

## Tears in Canvas Paintings: Resulting Stress Changes and Treatment

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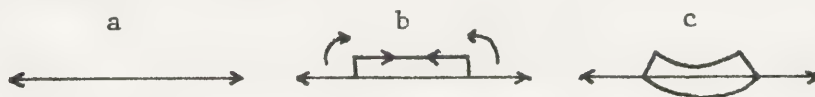
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## Introduction

Canvas paintings may be considered structures under tension. It is the tension which provides a stable, suitable surface for painting. Because the shortest connection (distance) between two points is a straight line, a stretched canvas forms a perfectly flat surface of high elasticity which will return to its previous condition following a local disturbance. This holds true for a homogeneous canvas only. If the continuity of the canvas is completely disrupted (cut or torn) it can no longer sustain its tension. The canvas becomes pulled out of shape and distorted.

In previous papers, the authors have shown what happens when the flat surface of a stretched canvas is disturbed by an asymmetrical load (See fig. 1) (1, 2). In this report, a complete disruption of the surface of a painting and its treatment are discussed.

Figure 1. Stretched canvas adjusts to an uneven load. 1a) Uniform stress. 1b) Uneven load (paint layer resists stress on one side). 1c) Surface bends to regain even distribution of stress.



## Stress propagation in a torn canvas painting

Figure 1 shows that a stretched canvas adjusts to uneven vertical loads by bending in such a way that the tension which is passing through it is evenly supported, or restrained, from both sides. This is shown on the schematic drawing of an area of impact (See fig. 2).



In figure 2, tension at the edges of the impasto (A and B) causes the canvas to bend downward and to distort the face of the painting.

No lasting results can be derived from using mechanical means such as ironing, suction, vapor-treatment, etc., in an effort to regain the original surface of a painting that has been distorted by an uneven load. The above treatments merely address the effects of the distortions, but do not address their underlying causes. Doerner's advice to treat cracking and cupping of paint is a step in the right direction. Applying stiff gouache paint to the reverse of a canvas will balance the forces that cause distortions (3). A modern version of Doerner's method has been reported by Hedley (4).

However, for this treatment to be effective, the layer of paint on the reverse would have to be symmetrical to the one on the face of the canvas in form, material, and properties. Since this is practically impossible to achieve, Doerner's suggested treatment might eventually introduce more asymmetry and greater distortions of the canvas than were present before. Therefore, the only remaining

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solution would be to line the distorted painting on a support stiff enough to withstand the forces generated by uneven loads.

A tear in a canvas painting creates uneven tension in the plane of the canvas in a fashion similar to impasto or cracks and in a direction perpendicular to the canvas. Here, however, the disturbance is more severe since the line of tension is completely interrupted at the tear. Such a sudden interruption must result in severe distortions in the plane of the painting unless the tear is closed in a way which assures that the original stress distribution is regained. Consequently, the material best suited to "bridge" a tear must have a similar resistance to tension as the original painting in order to prevent the continuation of stress concentrations and distortions. Any attempts to close a tear in a canvas painting with an adhesive that is less stiff than the canvas and/or the paint surrounding the tear will not yield the expected results. This is particularly true if a pliable adhesive with a low glass transition temperature ( $T_g$ ), such as BEVA or poly(vinyl) acetate, is used. These adhesives have larger "creep" than the canvas or paint. In order to join a tear properly and permanently, it is important to use an adhesive of similar stiffness as the canvas and often the paint as well. This requirement becomes obvious when looking at the face of the canvas rather than its cross section.

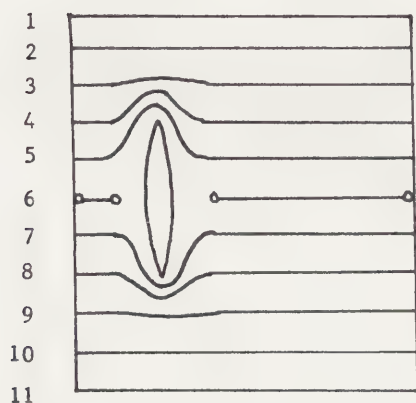


Figure 3. Stress propagation following a tear.

Figure 3 shows a stress diagram of a tear. The threads bearing the tension are cut by the tear. After the tear has occurred, the canvas will pull back and the edges of the tear will gape a little under stress. As a result, the material which was cut by the tear will relax. This is expressed in Figure 3 by stress line 6, which ends in zero. However, all this takes place after the tear has opened and the painting has had time to distort. On modern paintings without priming or sizing, it takes but a few days for such a distortion to form. Even in primed contemporary paintings, the priming and paint are so soft that similar distortions appear after a short time. If a tear in such paintings is not closed with an adhesive of similar strength to that of the contracting canvas, no satisfactory restoration is possible.

#### Stress concentration at the tear

The contemporary American Minimalist painting (1989) in Figure 4 was slashed accidentally in two places, with the bigger cut 80 mm long. When brought to our studio some 18 months after the accident, the clean slash had opened up to a gash 5 mm in width.

The importance of a swift, proper repair becomes still more evident in view of the following consideration: after the tear has occurred, at least part of the tension has to be supported by the remaining canvas, as shown by lines 3–5 and 7–9 converging at the ends of the tear (See fig. 3). This convergence is called "stress concentration" and can be expressed by the following mathematical formula (5):

$$S_c = S [1 + 2(L/r)^{0.5}]$$

where

- $S_c$  = stress at tip of the crack
- $L$  = length of crack
- $r$  = radius at the tip of the crack
- $S$  = stress at original uniform tension

Since the radius at the tips of the cracks in paintings is minute, the stress at the tip ( $S_c$ ) will be very large indeed. Under these circumstances, a crack would propagate rapidly were it not for the fact that the paint film is attached to its canvas. This is not the case for glass or ceramics where there is no additional reinforcement from a support. On the other hand, in a canvas painting a crack or tear will lengthen or widen only if the canvas is further stretched (increasing " $S$ ") or torn (increasing " $L$ "). However, the canvas, being overstretched by the stress concentration, "creeps" at the tips of the tear, thereby enlarging the radius( $r$ ) at the tip. The tear grows slowly in size, and the distortion of the canvas surrounding it increases if the tear is left unattended and not closed.



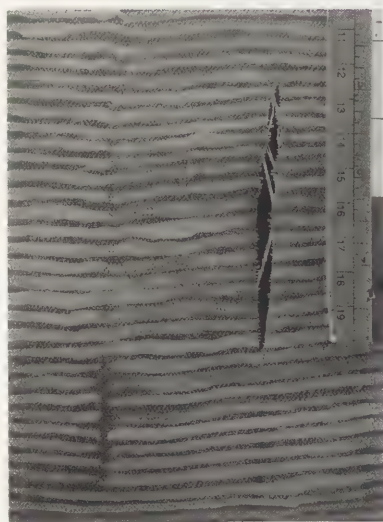


Figure 4a. Contemporary American Abstract (Minimalist), oil on cotton, 60×40 cm, before treatment.



Figure 4b. Same painting, following treatment.

If the painting is old, the canvas and paint are stiff and brittle. The surface of the canvas cannot stretch and distort as easily as in a modern or contemporary painting. Therefore, the stress concentrations at the tip of the crack or tear are more severe and the danger that the crack will propagate becomes greater. Propagation of a crack in an old painting can be reduced by temporarily securing its tips with tape.

For the preservation of old and modern paintings, it is essential to remove the stress concentrations first and to arrest the propagation of the tear. In Figure 3, stress concentration is generated because at least part of the tension which was previously borne by the fabric before it was torn must now be borne by the tips of the tear. To relieve the stress at the tips of the tear, the torn fabric must be made to carry again its full share of the load, or the same amount of tension stress as the rest of the canvas.

### Treatment of a tear

The conservator faced with the need to restretch a canvas in an area of a tear must bring the distorted canvas back into its original position first (See fig. 4). To do this, we have to bring the edges of the tear together as closely as possible to their original position. The manipulations required to achieve this goal are often time-consuming and complicated. Before embarking on this operation it is, therefore, essential to consolidate any loose paint. Usually, it is also better at this point to cut off any loose or protruding threads which might have been pulled out of the tear as a result of the impact that caused the tear. At the time of this writing, only epoxy can be considered to have sufficient strength or stiffness to substitute for the torn fabric or the stiff paint, as confirmed by Hedley's tests (6). Accordingly, for the preliminary consolidation, it is important to use adhesives which are compatible with epoxy, such as the traditional colletta or solubilized cellulose (7). If either adhesive cannot be used because of possible discoloration of the paint film and another adhesive has to be chosen, great care must be taken not to contaminate the edges of the tear with the consolidant. Following consolidation, the painting has to be removed from its stretcher to reduce the tension all over its surface.

When trying to correct distortions on modern paintings, particularly those on cotton supports, it is best to avoid direct application of moisture to prevent shrinkage. In spite of that, it is often useful to keep such a painting in a humid environment of about 60% relative humidity immediately prior to or during treatment. Since canvas pulls back (away) from the edges of the tear (and the tear opens as a result), extra canvas remains at the tips of the tear. When the edges are brought together, the surplus canvas buckles (See fig. 5, paper model). This buckling must be removed with heat before the tear is closed. Cellulose (canvas threads) and oil paints have a low T<sub>g</sub> and can be plastically deformed at relatively low temperatures. Stretching the canvas in the direction of the tear sometimes helps to reduce distortions, as does physical manipulation on a Mitka suction plate and local heating with a heat-blower (8). If the painting can take heat and pressure, hot irons and spatulas are, of course, helpful tools when trying to return a distorted surface to its original position.

It is often useful to attach the painting to a flat board covered with silicone-coated paper. This arrangement often enables the conservator to push the edges of the tear gently towards each other, and to keep them together in position with weights or thumbtacks. When the edges of the tear are completely aligned, the damaged area should be given a light heat treatment in order to remove any remaining planar distortions. Depending on the surface of the painting, this can be done either under low suction or by using a heated iron. Once their "best fit" is achieved, the edges of the tear should be secured with either BEVA Film(R) or self-adhesive labels. (Self-adhesive labels are preferable to adhesive tape because they are easier to remove, less elastic, and less likely to "creep." The tape is applied only to one side to permit application of the epoxy from the other side.)

The areas adjacent to the edges of the tear are then coated with diluted BEVA 371(R), taking great care to leave the edges themselves clean and uncoated.



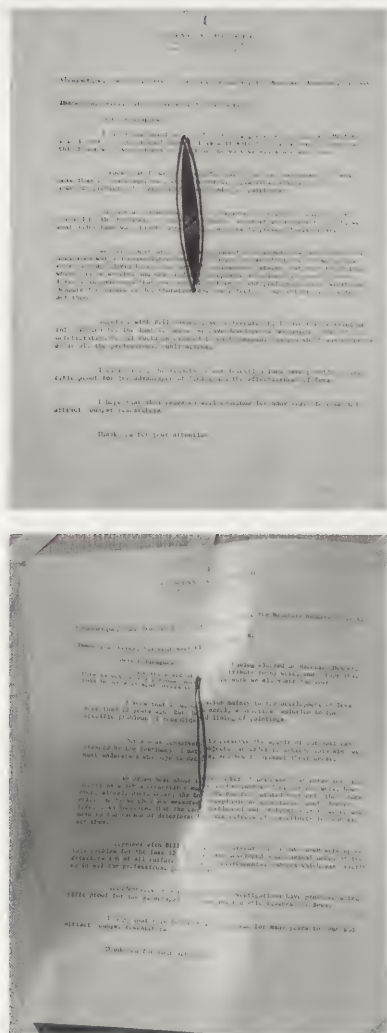


Figure 5. Paper model of a tear. (Paper was used because its stiffness helps demonstrate the distortions caused by a tear.) 5a) Cut-out area simulates a tear in a canvas. 5b) Efforts to reconnect the "open tear" cause the paper to buckle and distort.

(Because epoxy does not stick to BEVA, this coating will enable the conservator to remove any excess of epoxy which might spread to either side of the crack.) However, should any BEVA accidentally flow onto the actual edges of the tear, it is usually possible to remove by scalpel or a swab soaked in hexane or acetone.

The edges of the tear are then joined with full strength or slightly plasticized epoxy (9). The epoxy is often tinted to match the canvas or the background. However, epoxy resins tend to yellow and should only be used as underlayers which can be covered by an opaque layer of stable paint or gesso. The small Mitka suction plate serves very well to further secure the perfect alignment of the edges. Surplus epoxy should be removed using a scalpel while it gels and before it has time to set completely.

It is tempting to close a tear with a weaker or more reversible adhesive than epoxy. However, the strength of new linen or cotton is such that only the strongest adhesive will make restretching of the repaired canvas possible. Similarly, the stiffness of heavy layers of old paint requires a very hard, stiff adhesive to match it. A more flexible adhesive "gives" more under stress, making the repair useless. Still more important is the fact that a softer adhesive will have contaminated the edges of the joined tear, thus making further or future repairs much more complicated.

Even after the edges of the tear are exactly and seamlessly connected, warping and distortions frequently recur due to residual or newly generated stresses during the repair. Therefore, after closing the tears, it is advisable to remove these stresses as much as possible by giving heat and vapor-treatments on the vacuum hot table to the entire painting.

However, even a perfectly closed tear provides the surrounding paint film with only limited protection from stress concentrations. It is important for the repaired tear to be of approximately the same stiffness as that of the surrounding painting. However, this is impossible to achieve for every environmental condition to which the painting might be exposed in the future. Consequently, the joined tear will continue to cause stress and subsequent distortions of the canvas. It must be expected that even the best repair of this kind will eventually create distortions, such as bulges or dents, in the direction perpendicular to the canvas. Recurrence of such distortions can only be avoided if closing of the tear is followed by a lining of sufficient stiffness to absorb the small stress differences caused by the unavoidable divergence between the materials used to repair the tear and those of the painting itself.

### Conclusions

1. A stretched canvas can sustain uniform tension only as long as it is homogeneous.
2. A tear or cut disrupts the balance in the canvas and causes it to deform.
3. Such a tear or cut must be promptly "closed" using an adhesive of sufficient strength and stiffness to substitute for the torn fabric and paint.
4. Recurrence of distortions of the repaired canvas can only be avoided if closing of the tear is followed by a lining of sufficient stiffness.

### Acknowledgements

The authors wish to thank the Samuel H. Kress Foundation and its President, Dr. Marilyn Perry, for their financial and moral support for this research since its inception. The College of Architecture at the Georgia Institute of Technology has also provided continuous support and assistance. The generous contributions of expertise and resources by many other individuals and foundations are recognized and appreciated.

### Materials and Suppliers

Colletta. A mixture of carpenters' glue, water, molasses, vinegar, oxgall (90:75:22:60:10), and a small amount of sodium benzoate according to Mora (7).

BEVA 371(R), BEVA FILM(R), and other BEVA(R) products for conservation. Produced by Conservator's Products Company, Post Office Box 411, Chatham, NJ 07928 USA; telephone (201) 927-4855. In Europe, the name of my adhesive



was changed to Gustav Berger's Original Formula 371 to protect the genuine formula, because Lascaux is using the name BEVA for a product manufactured beyond my control. Dal Monte is the sole producer of G. Berger's Original Formula 371, as well as of other BEVA products (Dal Monte Renzo of C.T.S. s.a.s., Via Piave 20/22, 36077 Altavilla Vicentina (VI), Italy; telephone 0444/370362). I continue to test every batch of my formulations produced by Dal Monte.

Epoxy resins. Epoxy resins with a setting time of 4–12 hours are available from TALAS, 213 West 35th Street, New York, NY 10001-1996 USA; telephone (212) 736-7744. In Europe, the resins are available from C.T.S., as above.

Self-adhesive labels. Produced by Avery Label Company, Monrovia, CA 91016 USA. Also available in stationery stores.

Solubilized cellulose, such as methyl cellulose. Available from TALAS, New York, USA.

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## Abstract

This paper provides a survey of previously described transparent linings of paintings. This is followed by the description of a transparent cold-lining of a transparent oil painting on a starch-impregnated cotton canvas. The cold-lining was done with Plextol B 500 on a polyester fabric Polymon PES 65/36, using a low-pressure table.

## Keywords

Transparent lining, cold-lining, transparent painting, polyester fabric, Polymon, Stabiltex, Plextol B 500, solvent re-activation, low-pressure table

## Transparent Cold-Lining of a Transparent Painting

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## Introduction

The conservation of paintings has undergone rapid development, particularly within the past decades. This is mainly due to the advent of synthetic polymers in, for example, binding agents. The development has not been nearly as rapid for painting canvases, especially as regards transparent support canvases.

The earliest described transparent back support was made on a rigid vinyl sheet with a copolymer vinyl resin. This was described by S. Keck in 1940 (1). About 20 years later, A. Boissonnas introduced a wax-lining made on a fiber glass fabric (2). For a long period of time, this type of lining support was prevalent. Subsequently, the method was improved by E. Pacoud-Reme, who described in 1981 how to produce the translucent pure wax/resin mixture for transparent linings (3).

However, fiber glass fabric for lining failed to provide sufficient support to prevent the return of planar distortions in severely distorted surfaces. To circumvent this problem, G. Berger used a sandwich design of Mylar, fiber glass fabric, and BEVA(R) (4). Berger later described several different transparent linings with BEVA(R) and fiber glass canvases. As a replacement for sandwich linings, in 1981, Albert Albano described how to support the fiber glass canvases with Akemi, a transparent flowing polyester resin (5).

Suitable fiber glass canvases are rarely available, however, in widths exceeding 1.2 m (47.24"). To my knowledge, fiber glass canvases exceeding 1.2 m are of such heavy-duty quality that their transparency quality is, unfortunately, much impaired.

Previously, if you wanted to avoid joins and nevertheless wanted to make a transparent lining, these two objectives have been almost incompatible when the smallest dimension of the painting exceeded 1.2 m. I have, therefore, investigated this matter in regard to what other types of transparent canvases are available.

Thin polyester canvases have a very satisfactory transparency. The Schweizerische Seidengazefabrik is a manufacturer of both the monofilament Polymon canvas and the multifilament Stabiltex canvas. They are available in widths up to 2.7 m (66.92"). Monofilament means that each thread has been produced from one fiber, whereas the multifilament quality has been produced from several thin fibres spun into one thread.

I found that the monofilament Polymon canvases had the highest transparency. Contributing to this, in the case of multifilament threads, there is a greater risk that air pockets are formed in the thread between the spun fibers. Furthermore, the Polymon canvases are slightly more rigid than the Stabiltex canvases. Thus, the Polymon canvases work better in preventing a return to planar distortions.

Polymon-fabrics can be obtained in several finenesses of weave. Thread diameters range from 27 micrometers for the finest fabric to 1000 micrometers for the coarsest fabric (6).

There are several advantages of Polymon-fabrics, according to the manufacturer:

1. Tensile strength: (Dry) From 45–60 kg/mm<sup>2</sup> (65,000–85,000 psi); (Wet) 100% of dry strength.
2. Dimensional stability: Excellent.
3. Low moisture-absorption: At 65% RH and 25°C approximately 0.4%; at 95% RH and 25°C approximately 0.5%.
4. Chemical resistance: Polyester fabrics are highly resistant to attack by solvents



and chemicals. Only some phenolic compounds and hot nitrobenzene dissolve the fabric.

5. Durability: Polymon-fabrics are not affected by ultraviolet radiation and have a good resistance to oxidizing agents. In addition, they have an extremely good resistance to decay, bacteria, etc.

### Conservation of a transparent painting

The painting in this study originates from the masonic-related society known as "Kjæden" (the Chain). It is an allegoric painting attributed to a Danish painter, Nicolaj Abildgaard, in 1783.

### Technique

The painting is circular, measures 2.53 m (99.6") in diameter, and is stretched tightly onto a collapsible stretcher. The painting is painted with oil paint on a starch-impregnated cotton canvas. This type of support is normally used as painting ground in the transparent painting technique, as it is much more translucent than gesso-grounded linen canvases.

In the transparent painting technique, each individual layer of paint in the painting has to be transparent in order to attain the transparency effect. Light and dark color areas are created by varying the thickness of the paint layer. Thus, thick paint layers will produce dark colors.

Transparent paintings are not automatically translucent. While paintings generally are to be viewed in reflected light, transparent paintings should be viewed in a mixture of transmitted and reflected light. The greatest effect is attained with transmitted light only. This means that the materials used for the conservation of such paintings have to meet special requirements. All materials have to be as transparent as possible.

### Condition

The cotton canvas was in a very critical state prior to treatment. The canvas threads were very deteriorated and, therefore, they broke easily. The left half of the painting had a cross-shaped tear running 80 cm (31.5") in the vertical direction and 45 cm (17.7") horizontally. The damage had been secured locally with patches earlier on, but these had prevented the light from passing through. This part of the painting, therefore, appeared black. In addition, the painting had several large and small tears and holes (See fig. 1). The starch was stable, but forms of illumination used in the past, such as tallow candles, oil lamps, and gas lamps, had discolored the reverse side of the canvas.

### Conservation

The largest tears of the painting were locally secured with polyester fabric Polymon PES 65/36 impregnated with BEVA(R) 371. Minor tears were secured with dried BEVA(R) by bonding the edges of the tears with tiny pieces of adhesive and a hot spatula.

The painting was then mounted on a stretcher and humidified in order to subsequently remove planar distortions on a low-pressure table (7). After humidification, it was remarkable how the crumbled canvas regained its previous strength. Next, the reverse side of the painting was cleaned with water with an admixture of Agepon.

The transparent painting had been painted on a starch-impregnated cotton canvas. In order to prevent the binding agent of the cold-lining from penetrating the painting, the reverse side of the painting was sized with corn starch. The polyester fabric Polymon PES 65/36 was stretched onto a work frame, and then five thin coats of Plextol B 500 were applied (8). Each coat was allowed to dry for 12 hours between applications. The binding agent was next activated with brush-applied toluene after which the Polymon fabric was placed on the reverse of the painting. This cold-lining took place on a low-pressure table.

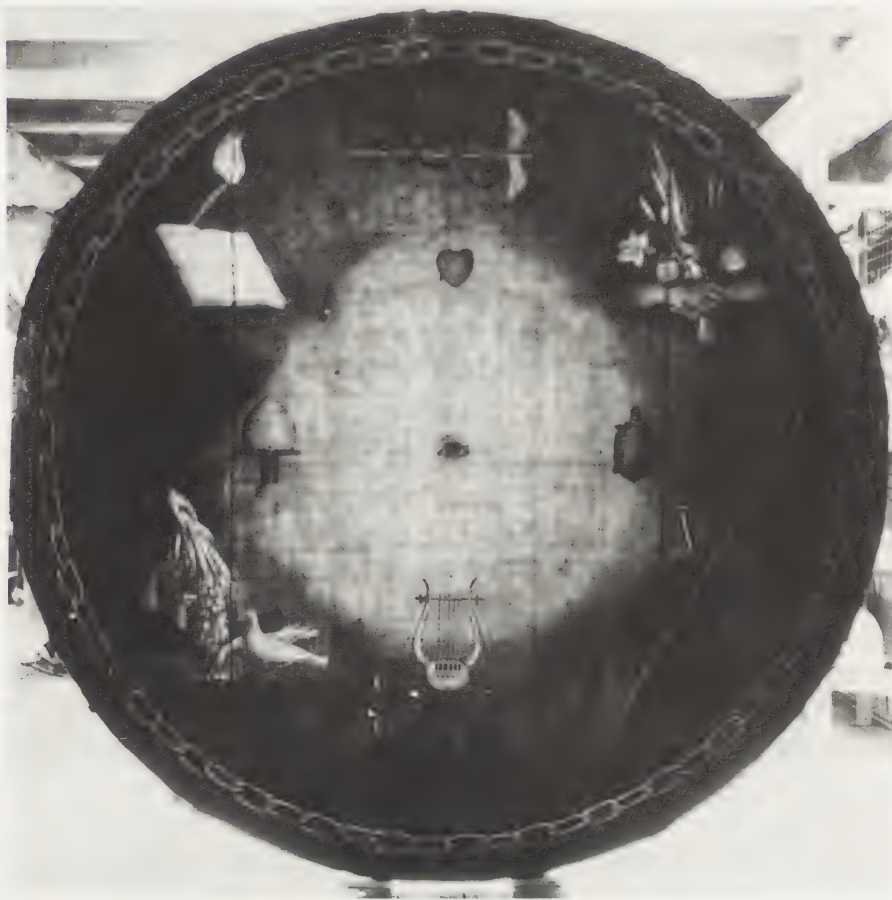


Figure 1. Transparent painting before conservation.



Figure 2. Transparent painting after conservation.



Schweizerische Seidengazefabrik has several types of polyester fabrics, but in this particular case I found that the polyester fabric Polymon PES 65/36 was the most suitable. Figure 2 shows the painting after conservation.

### Conclusions

The results of the conservation treatment of the transparent painting described in this paper showed that the thin polyester fabric Polymon PES 65/36 was very suitable for a transparent lining. The polyester fabric is available in widths up to 2.7 m (66.92"), should treatment require large, unjoined pieces of fabric to line paintings.

The painting was restored in the autumn of 1989. Since that time, no changes in the painting surface, structural distortions, tears, or yellowing of the materials used have been observed.

### Acknowledgements

I wish to thank "The National Workshops for Art & Crafts, Old Dock Warehouse", Copenhagen for making the conservation facilities available during this conservation process. I also wish to thank conservator Mr. Steen Bjarnhof for making it possible to use these very excellent facilities.

### Materials

Stabiltex & Polymon. Schweizerische Seidengazefabrik AG Zürich, Grütlistrasse 68, Postfach, CH-8027 Zürich 2, Switzerland.

BEVA(R) 371. Heat-activated adhesive (composition). Lascaux Restauro. Alois K. Diethelm AG, Farbenfabrik, CH-8306 Brüttisellen, Schweiz.

Plextol B 500 (methyl methacrylate copolymer emulsion). Known in USA as Rohamere B 500. Röhm GMBH Chemische fabrik, Postfach 4242, Kirschenallee, D-6100 Darmstadt 1, Germany.

Agepon. Wetting agent (composition). Agfa-Gevaert, D-5090 Leverkusen 1, Germany.

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2. Alain Boissonnas. "Relining with Glass-Fiber Fabric," *Studies in Conservation* 6 (1961): 26-29.
3. E. Pacoud-Reme, "Trois cas de rentoilage transparent faits par G. Ten Kate au service de la restauration de peintures des musées nationaux" (Paper delivered at the Sixth Triennial Meeting of the International Council of Museums Committee for Conservation, Ottawa, 1981), 2/11-1.
4. Gustav A. Berger, "Unconventional Treatments for Unconventional Paintings," *Studies in Conservation* 21, no. 3 (1976): 115-128.
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6. Schweizerische Seidengazefabrik AG Zürich, Grütlistrasse 68, Postfach, CH-8027 Zürich 2, Switzerland.
7. Volker Schaible, "Reflexions sur la formation de cuvettes à la surface des peintures sur toile" (Paper delivered at the Ninth Triennial Meeting of the International Council of Museums Committee for Conservation, Dresden, 1990), 139-144.
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## Résumé

Une table à basse pression munie d'un système de contrôle et d'acquisition permet de créer des conditions particulières de traitement, comme par exemple une tension constante, et d'en garder une mémoire précise et objective. Le système peut constituer un moyen de caractérisation relative du tableau en vue de l'évaluation future des traitements effectués.

## Mots clefs

Table à basse pression, fiche d'acquisition, ordinateur, contrôle de tension, châssis à expansion

## Acquisition de données et contrôle par ordinateur dans les traitements à basse pression

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### Introduction

On aurait tort de considérer l'utilisation d'un ordinateur pour un appareil à basse pression comme un gadget, ou au plus un accessoire. Si dans le passé nous avons eu plusieurs exemples où le soi-disant progrès technique n'apportait pas de réels avantages, toutefois l'expérience nous a démontré qu'un tel appareil apporte des bénéfices importants. Il garantit un système de contrôle des forces en jeu sophistiqué et il permet d'accomplir des fonctions que le plus habile des restaurateurs ne saurait faire, comme par exemple un contrôle efficace de la tension.

Les techniques de relaxation à basse pression utilisent les mêmes facteurs actifs que la méthode traditionnelle à la pâte (chaleur, pression, humidité et tension). Cela constitue un point de rencontre important entre tradition et innovation, toutefois, leur emploi calibré et contrôlé apporte des résultats fort différents comme on connaît depuis plusieurs années (1).

Dans ces techniques on abandonne décidément l'idée de traiter des tableaux d'époque et de nature apparemment semblables avec un procédé identique, basé principalement sur l'impregnation et le rentoilage par un adhésif, soit naturel soit synthétique, où le tableau prend similitude avec les caractéristiques de l'adhésif d'impregnation et se comporte en conséquence. Au contraire, avec les procédés à basse pression, le tableau et sa capacité de réaction par rapport à certaines contraintes, peuvent rester intacts. Celles-ci deviennent l'aiguille de la balance dans les choix du restaurateur puisque le tableau réagira seulement en fonction de sa structure. Ce qui frappe le plus c'est la sensibilité que montre le tableau vis-à-vis des changements climatiques que l'on lui fait subir au cours du traitement et le "caractère" que chaque tableau exprime en y réagissant. Au fait, en raison d'une sensibilité accrue vis-à-vis du problème de l'impregnation par substances filmogènes de la structure picturale, la table à basse pression est devenue un instrument irremplaçable dans le cas des tableaux modernes et contemporains, de même que pour les peintures anciennes qui n'ont pas été rentoilées.

### Objectifs du système

Le premier but fut de créer une sorte de "mémoire" de ce qui se passait au cours d'une session de travail, afin d'enregistrer de façon objective les événements et montrer les conditions réelles de travail pour balayer le champs du doute et de la méfiance envers cette technique non conventionnelle. Le second but fut d'accomplir des mesures précises afin de collecter en un temps minimum même des phénomènes d'ampleur très réduite. Le restaurateur dans le rentoilage à la pâte fait confiance à ses sens pour établir si la chaleur est ou n'est pas excessive; si la pression est trop grande et s'il faut la diminuer. Avec les techniques à basse pression, si nous considérons la petitesse en valeur absolue des forces employées, nous nous rendons compte que nos sens seuls ne sont plus suffisants pour conduire cette tâche de contrôle. De même, une considération s'impose: les nouveaux matériaux utilisés dans la conservation des peintures sur toile à différence des adhésifs d'origine animale changent fortement leurs caractéristiques en fonction des conditions d'application et d'activation. Comment établir dans un futur plus ou moins proche la justesse de l'adhésif et de la méthode d'intervention choisis sans avoir toutes les données du problème?

Enfin, si température, pression et humidité sont contrôlées de façon satisfaisante par un grand nombre d'appareils, la tension que l'on confère au tableau à l'aide de bandes de papier ou d'un châssis mécanique à expansion est contrôlée de façon très empirique par l'opérateur, qui dans beaucoup de cas se trouve dans l'impossibilité de la modifier de façon efficace au cours du traitement.





Fig. 1 La table à basse pression. La plaque a été noircie par galvanisation afin de mieux dissiper la chaleur.

Il apparut alors, que le meilleur moyen pour satisfaire à ces exigences était de réaliser un système qui relevât les données de température, humidité, pression et tension chaque seconde: on recourut alors à un ordinateur avec une fiche d'acquisition, un programme dédié et des sondes électroniques.

L'utilisation de l'ordinateur permet d'ordonner dans une archive, la fiche habituelle du tableau (description de l'objet, état de conservation, interventions effectuées et prévues etc.) et toutes les sessions de travail sur l'appareil (conditions climatiques du milieu, chaleur, pression, humidité, tension) de façon à pouvoir effectuer par la suite une analyse complète du traitement et de ses effets.

Pour mieux évaluer l'utilité de l'appareil, on decida de le construire avec des doubles commandes (manuelles et automatiques) et un double système de contrôle: l'un manuel, l'autre automatique par ordinateur. Dans ce dernier cas, le thermostat électronique du système manuel, qui est physiquement indépendant du système automatique, prend les fonctions de contrôle en arrière-plan de la température. Ainsi, dans le cas d'un dysfonctionnement du programme ou de l'ordinateur, le thermostat intervient et contrôle la chaleur de manière autonome.

### Le système d'acquisition et de contrôle

Aujourd'hui toutes sortes de sonde sont disponibles avec un signal électrique en sortie, ce qui permet de les connecter à une fiche d'acquisition de l'ordinateur (après avoir convenablement conditionné le signal) et d'obtenir ainsi une grande flexibilité d'emploi. Les sondes électroniques sont plus précises, plus économiques et ont un temps de réaction moindre par rapport aux sondes traditionnelles. Le rôle de la fiche d'acquisition est de convertir le signal électrique (analogique) provenant de la sonde en un numéro binaire (digital). Par exemple une sonde de température avec gamme 0-100°, fournira un signal qui correspondra pour l'ordinateur à un intervalle numérique de 0 à 32000, la résolution étant donnée par la division de 100 degrés par 32000. Théoriquement le système pourrait relever une différence de l'ordre d'un millième de degré, mais en réalité l'erreur (1% sur la gamme) est donnée par le capteur de température. De même l'ordinateur peut faire l'inverse; c'est-à-dire, produire un signal électrique soit digital (allumé/éteint), soit analogique (4-20 milliampères) en sortie pour le réglage de dispositifs externes (réchauffement, humification etc.). Cette grande précision permet de réaliser aisément et économiquement des mesures même complexes comme celles avec estensimètres ou celles de type spicrométrique (évaluation de la perte d'humidité de la toile au cours du traitement). Une fois que les données arrivent à l'ordinateur et qu'elles sont converties dans son langage, il faut les organiser pour le contrôle et l'acquisition. C'est le programme qui s'en occupe. Nous avons choisi d'écrire nous-mêmes le programme en utilisant un langage simple (Microsoft Quickbasic) pour être en mesure d'apporter à tout moment les modifications nécessaires. Une fois de plus les restaurateurs doivent penser eux-mêmes à leurs instruments. La possibilité de charger différents programmes dans l'ordinateur modifie les fonctions de l'appareil, permettant de conduire facilement des épreuves expérimentales, des traitements particuliers ou même une utilisation disjointe de l'appareil à basse pression.

En traitant pour la première fois un tableau, la session de travail commence par la création de la fiche du tableau. On peut y ajouter les valeurs maximales de température, pression et humidité. Le programme de contrôle prendra ces valeurs comme limites, ensuite au cas où l'opérateur cherchait à établir des valeurs plus hautes que celles-ci, un message d'erreur apparaîtrait pour défendre cette opération. Pour des fins didactiques, on peut établir aussi automatiquement des valeurs de consigne infranchissables à partir de données de la fiche comme technique picturale, époque, état de conservation, etc.

Le fonctionnement est simple; il y a un menu où on saisit les valeurs de consigne de la température et de la dépression que l'on veut atteindre. On peut aussi les subordonner à un compteur de minutes. La pression, la montée de la température ainsi que le refroidissement sont programmables par échelons d'une durée variable.

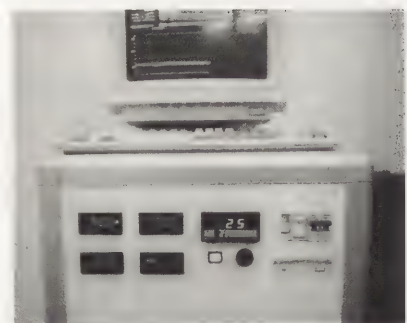


Fig. 2 L'unité de contrôle de l'appareil avec les indicateurs de température, humidité relative, dépression et le thermostat.



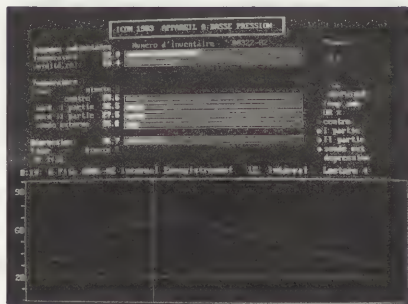


Fig. 3 Ce qui apparaît sur l'écran pendant la session de travail. Le graphique cartésien montre les courbes d'un réchauffement rapide de 35° à 65° et de 65° à 75° avec contrôle par thermorégulateur et le refroidissement de 75° à 30° en 30 minutes. La ligne verticale correspond à un temps de 14 minutes.



Fig. 4 Le basculement de la table en position verticale. On voit le mécanisme de pivot avec les ressorts à air comprimé.

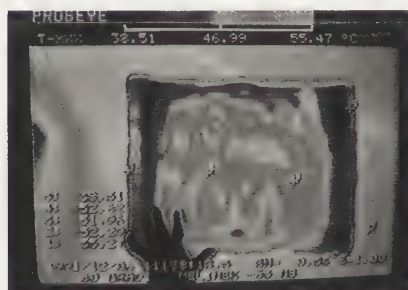


Fig. 5 Thermographie d'un tableau du XIX<sup>e</sup> siècle huile sur toile de lin mince traversé par l'air. Les zones plus claires sont plus chaudes car elles correspondent à des épaisseurs importantes de couleur qui empêchent le passage de l'air.

Sur l'écran les informations relatives aux sondes sont représentées soit en forme numérique soit en forme graphique par des barres horizontales (Fig.3); au bas de l'écran on trouve la représentation des mesures sur le temps dans un graphique cartésien où l'on peut soit varier l'intervalle de temps entre chaque mesure, soit sélectionner les sondes à montrer sur le graphique ainsi que celles à enregistrer sur le disque dur de l'ordinateur.

Le graphique tracé en temps réel est extrêmement utile. Lorsqu'on travaille sur le tableau il est plus important d'avoir une image du cours du réchauffement ou de l'humidification plutôt que des chiffres isolés et anonymes. Il est possible de revoir avec l'intervalle de temps souhaité les graphiques enregistrés auparavant.

A l'aide d'un commutateur on passe du contrôle automatique au manuel, un message exige une confirmation par l'opérateur à cause du changement du système de contrôle utilisé.

### La table à basse pression

La table a une structure en acier et aluminium, sa dimension utile est de 150 × 250 cm. Le plan de travail est formé par une plaque en aluminium de 5 à 8 mm d'épaisseur entièrement percée avec des trous à deux diamètres pour une meilleure distribution de la dépression grâce à l'effet Venturi. Il y a la possibilité de basculer en position verticale pour rendre plus facile la mise en place des tableaux grands ou fragiles, ainsi que pour travailler plus aisément (Fig.4). La dépression est obtenue à l'aide d'une turbine de grande portée, un régulateur électronique de vitesse permet de la régler à moins d'un millibar près; la pression maximale (plaque scellée) est d'environ 140 millibars.

On a considéré avec soin le système de réchauffement: quiconque a travaillé sur les tables chauffantes, sait que rarement le réchauffement est homogène sur toute la surface de la plaque. Normalement, les tables à basse pression réchauffent la plaque par radiation, ainsi, le système de véhiculation de l'air aspiré ou les supports de la plaque perforée forment une chambre à air avec une considérable inertie thermique. Il en résulte une difficulté pour contrôler convenablement la température même en utilisant un thermostat électronique (ce dernier ira facilement se surchauffer). Nous avons aussi contrôlé à l'aide d'un appareil thermographique à haute résolution (0.1°) l'uniformité du réchauffement sur un appareil de vieille conception. Comme on s'y attendait, toutes les parties de la structure avec une bonne conductibilité thermique touchant la plaque perforée (aluminium) dissipaient la chaleur, ce phénomène intéressait soit les bords, soit la grille de soutien et de distribution de l'air. Aux bords, on avait jusqu'à 12-16% de température en moins, en correspondance de la grille la différence était de 1-2 %, mais cette valeur tendait à augmenter lorsque la dépression était active. Dans le cas où l'on voudrait chauffer et en même temps maintenir sous pression le tableau sans le couvrir avec le Melinex des tableaux très poreux, on aurait des problèmes à cause de l'énorme quantité d'air qui passe à travers le tableau et qui refroidit très rapidement la plaque. De plus, il sera fondamental alors, que le sensor soit en correspondance du tableau sous peine de régulations thermiques désastreuses.

L'emploi de la thermographie nous a montré que le tableau même dissipe de façon importante et inattendue la chaleur. Les zones de couleur avec de grosses quantités de pigment à poids atomique élevé restaient de 5-8% plus froides que la température de la plaque, en activant l'aspiration le phénomène s'inversait (Fig.5).

On a observé aussi qu'appuyer sur la plaque près du tableau des masses importantes comme des sachets de plomb ou de sable pour bloquer la feuille de Melinex, comporte jusqu'à 20 % de perte de chaleur dans les zones limitrophes et sur les bords du tableau. Nous avons adopté une solution qui améliore considérablement le réchauffement et la possibilité de maintenir une certaine température même en activant la dépression. Il s'agit de résistances électriques convenablement isolées, posées dans un fraisage pratiqué dans la plaque qui passent entre les rangées de trous à une distance d'un centimètre l'une de l'autre (Fig.6). En éliminant le volant thermique (l'air entre élément chauffant et la plaque), le



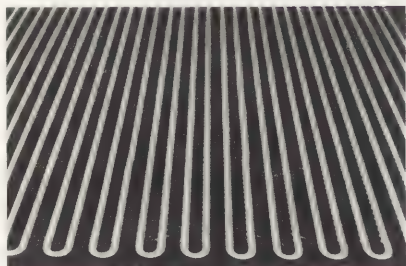


Fig. 6 La plaque d'aluminium vue par dessous avec les résistances électriques posées dans le fraisage.

### Considérations sur l'emploi de l'appareil

La possibilité d'un emploi soit "traditionnel" avec le contrôle manuel soit "intelligent" avec l'ordinateur a mis en évidence les caractéristiques propres de ce dernier:

La régulation de la température même dans des situations "critiques" qui mettaient en crise le régulateur électronique était fort efficace, en plus, en ayant trois capteurs de température sur la plaque et un à l'extérieur à mettre sur la surface du tableau, on pouvait attribuer à chacun d'entre-eux ou à leurs moyennes le rôle de repère pour la régulation de la température. Le contrôle de la dépression aussi est efficace. De plus il est possible de maintenir constante la dépression, même si la difficulté du passage de l'air aspiré à travers le tableau change en fonction d'une variation de sa porosité ou d'une manipulation de l'opérateur. Si la dépression chute, le programme augmente la vitesse de la pompe en la compensant.

La sensibilité du capteur de dépression (1/10 de mbar), permet d'avoir une idée de la quantité d'eau absorbée par la structure de certains tableaux pendant l'humidification; sur la plaque on met un Melinex avec une fenêtre où l'on place le tableau sec. A une certaine vitesse de la pompe on aura une certaine dépression. Après humidification, l'air rencontrera plus de difficulté à passer à travers le tableau à cause de l'eau absorbée (l'eau faisant bouchon). La dépression augmentera pour retourner ensuite près de la valeur initiale. De la même façon, on peut mesurer l'impregnation créée par l'application d'un adhésif en évaluant la qualité du film formé à l'intérieur du tableau.

On préfère l'humidification lente (2) aux systèmes qui utilisent la chaleur pour humidifier car souvent ceux-ci donnent lieu à des condensations fort dangereuses. De même un compliqué système clos d'humidification à circulation d'air a été testé, mais celui-ci n'a pas apporté d'avantages concrets.

La représentation graphique de l'humidification est extrêmement intéressante car elle est en fonction de la perméabilité du tableau à l'humidité. Comme pour d'autres méthodes, la forte humidification oblige, afin de contenir les risques de variation dimensionnelle, à mettre la toile en tension pendant le traitement avec un châssis mécanique à expansion.

### Le système de tension actif

C'est un châssis composé d'un tréfilé en aluminium et profil en bois monté sur des pièces à équerre en aluminium massif qui présentent aux bouts un morceau avec une crémaillère, sur laquelle s'enclenche perpendiculairement un engrenage fixé à l'arbre d'un moteur à courant continu ("stepper motor"). Ce type particulier de moteur à aimants permanents, permet de diviser un tour complet en une succession de 400 fractions, ce qui donne une précision dans le déplacement de 8/100 d'un millimètre; une fois dans la position voulue, le moteur reste bloqué automatiquement. Une solution plus économique consiste à employer des motoréducteurs à engrenage. Chaque angle du châssis peut avoir un ou deux moteurs qui en constituent des points d'expansion. Entre la fin de l'équerre et la partie avec la crémaillère se trouve un petit senseur de pression connecté à la fiche d'acquisition qui fournit un signal en courant.

On agrafe le tableau sur la partie en bois du châssis à l'aide de bandes de tissu non hygroscopique collées aux bords de la toile avec une émulsion acrylique (Lascaux 498 20x) (Fig.7). On lance le programme de contrôle qui réglera la tension sur une valeur standard (Fig.8). Dès ce moment la tension du tableau est maintenue constante ou du moins reste à l'intérieur d'un intervalle qu'on détermine. Cette dernière peut être fixe ou variable en fonction du temps et des changements extérieurs comme l'application d'un adhésif ou l'humidification.

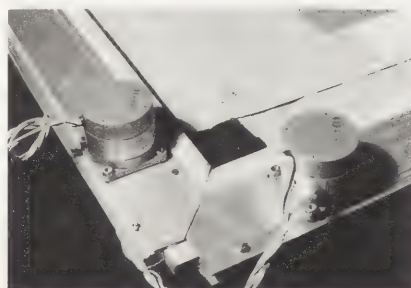


Fig. 7 Vue d'un angle avec deux moteurs pour l'expansion, un tableau de 1939 de Anastasio Soldati est monté avec des bandes de toile.

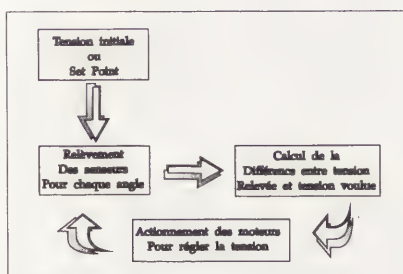


Fig. 8 Représentation du fonctionnement du programme de contrôle de la tension.

C'est une caractéristique particulièrement intéressante car lors de l'humidification lente, on élimine d'une part les risques d'élongation de la toile par traction excessive, et d'autre part le soulèvement de la couleur par contraction du support.

On peut établir toute une série de nouveaux types de traitements, basés sur une plastification douce de la pellicule picturale par la chaleur et l'humidité en relation à des changements programmés de tension. C'est un travail tout nouveau, peut-être une nouvelle méthode. Nous sommes confiants quant à des résultats intéressants à moyenne échéance, les débuts sont encourageants.

### **La caractérisation du tableau**

En établissant des conditions standard, on peut caractériser l'état présent du tableau. Cette caractérisation sera relative à l'objet et non pas absolue, mais elle permettra d'évaluer l'impact des interventions futures et de la dégradation apportée par le temps.

Avec le système décrit, on peut relever le taux d'absorption de l'humidité du tableau de même que son comportement dimensionnel pendant les variations hygrométriques. Tout cela, non pas au cours d'une expérience particulière mais pendant les séances normales de relaxation structurale sur la table à basse pression.

La grande flexibilité du système permettra d'y intégrer n'importe quel capteur et de le mettre en relation avec n'importe quel aspect du fonctionnement de l'appareil, ce qui deviendra un paramètre ultérieur d'évaluation.

C'est peut-être un premier pas vers la solution d'un grand problème dans la restauration des tableaux sur toile: la difficulté d'évaluer l'état du tableau en fonction de l'opportunité d'une intervention, ou bien en fonction de la qualité de cette intervention, à cause du manque d'un moyen de caractérisation quelconque qui ne soit pas basée uniquement sur nos sens et nos opinions.

La plupart des théories sur les phénomènes inhérents aux tableaux sont accompagnées de démonstrations expérimentales conduites sur des échantillons ou des facsimiles de tableaux. Vu les variables diverses qui déterminent l'état d'un tableau (la technique picturale, la dégradation, les restaurations antérieures), on peut légitimement se demander si cette approche est correcte, puisque même deux tableaux exécutés en même moment et avec la même technique présentent souvent après vieillissement des conditions de conservation très inégales. A notre avis, il est plus utile d'avoir une information peut-être plus statistique, que l'on ne peut donc assumer comme pièce à conviction dans la démonstration d'une théorie, mais plus proche de la réalité car elle se réfère à un grand nombre de tableaux.

### **Conclusion**

Nous croyons qu'un appareil contrôleur et enregistreur pourrait devenir un moyen de connaissance, puisqu'il permet de sauvegarder ce patrimoine qu'est la mémoire sensorielle du restaurateur. Ce n'est pas tout déléguer à une machine, bien au contraire.

L'ordinateur est un aiguillon à connaître davantage le tableau. Ce n'est qu'à travers la connaissance des nouvelles technologies que nous pouvons en extraire les moyens pour résoudre en partie nos problèmes ainsi qu'approfondir la connaissance des tableaux.

Il y a un paradoxe dans ce que la table à basse pression ne soit pas encore adoptée de façon massive dans des pays comme la France ou l'Italie, où la méthode traditionnelle de rentoilage à la pâte est en quelque sorte proche de la méthode à basse pression. En Italie, si d'un côté il y a eu une étude critique profonde sur les problèmes du nettoyage et de la réintégration picturale, avec l'adoption d'une méthodologie à cet égard qui a été aussi avancée que critiquée; par ailleurs dans l'intervention structurale des peintures sur toile, la discussion théorique semble arrêter sur la prise de conscience des limites du rentoilage à la pâte faite par Giovanni Urbani en 1972 (3). Il se pourrait que le rejet historique de l'utilisation de la table chauffante avec adhésifs fusibles en soit en partie la cause, mais aussi en égard à la faible sensibilité envers les concepts de moindre intervention, nous



déduisons qu'on préfère le rentoilage à pâte par prudence puisque on connaît désormais ses limites et ses dégats, mais on les accepte tout de même. Notre intention dans la réalisation de cet appareil a été aussi de commencer à introduire le mieux possible cette méthode en Italie. Les premiers résultats arrivent; aujourd'hui deux centres publics de formation des restaurateurs dans le nord de l'Italie ont adoptée cette méthode.

### Références

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2. Création avec une feuille de Melinex d'une chambre à deux climats, un saturé d'eau (tissu mouillé), l'autre avec le tableau à humidité relative ambiante séparés par un élément poreux non hygroscopique (mousse de polyuréthane). Par différence de pression de vapeur, les deux climats après un temps variable, s'équilibrent, on laisse le tableau à plus de 90% d'humidité relative jusqu'à ce que la couche picturale soit assouplie.
3. G. Urbani, "Problemi di conservazione", SIV, Bologna, 1972.

### Bibliographie

1. G.A. Berger and W.H. Russel, "An Evaluation of the preparation of canvas paintings using stress measurements", *Studies in Conservation*, 33, n°4 (1988), 187-204.
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3. G.A. Hedley, C. Villers, R. Bruce-Gardner, R. Macbeth, "A new method for treating water damage flaking", *Preprints* (ICOM Committee for Conservation 9th Triennial Meeting, Dresden, 1990), 119-123.
4. V. Schaible, "Reflexions sur la formation des cuvettes à la surface des peintures sur toile", *Preprints* (ICOM Committee for Conservation 9th Triennial Meeting, Dresden, 1990), 139-144.
5. M. Scharff, "Rapport om konstruktion af en lavtryksramme", Konservatorskolen, Det Kongelig Danske Kunstakademi, 1982.

## Abstract

Peel testing can assist in determining the suitability of a lining-adhesive system. This paper describes peel testing of wax-resin and BEVA 371 lining adhesives with various lining supports. Wax-resin bond strengths with untreated lining supports ranged between 715 N/m and 67 N/m and were mainly dependent on the surface texture of the lining material. BEVA bond strengths with untreated lining supports ranged between 1476 N/m and 211 N/m. Repeat BEVA samples, prepared at a later date, but as similarly as possible to earlier samples, had different bond strengths. Thus, small differences in preparation and lining conditions produced major differences in peel strength. The effect of pretreatment of selected lining supports is discussed. Studies on the effect of peel configuration, peel rate and ageing on peel strength are mentioned. It is recommended that peel tests be used only as guidelines rather than absolute quantitative measurements, as small differences in procedure can produce large differences in bond strengths.

## Keywords

Lining, painting, wax-resin, BEVA 371, peel test, linen, polyester, sailcloth, glass fibre

## Ongoing Research in the CCI Lining Project: Peel Testing of BEVA 371 and Wax-Resin Adhesives with Different Lining Supports

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## Introduction

The work described in this paper is part of an ongoing project at the Canadian Conservation Institute (CCI) on the behaviour of lined paintings. The initial phase of this project, reported at the 1987 ICOM Committee for Conservation meeting in Sydney, involved the measurement of the mechanical properties of model paintings under a variety of environmental conditions.<sup>1</sup> The current work investigates the bond strength of a few selected lining systems, using 180° peel tests.<sup>2</sup> To assess the ability of a lining system to minimize defects in a painting, the third phase will investigate the response of lining supports and lined model paintings to applied strain and to a variety of environmental conditions.

Peel tests assist in determining the suitability of a lining adhesive system. Information is provided not only on the strength of the bond between the canvas and the lining support, but also on the nature of the bond, its evenness and location of failure. Although the delamination of a lining is the result of a complex interaction of forces, peel strength is often chosen as an indicator of the bond strength under the stresses to which a painting is exposed.<sup>3</sup>

## Experiments

In these tests, model paintings were lined onto twenty-six lining supports using wax-resin adhesive and twenty-three using BEVA 371.

### *Sample preparation:*

Samples were cut and prepared according to ASTM D 903 "Peel or Stripping Strength of Adhesive Bonds" and ASTM D1682-64 "Standard Test Methods for Breaking Load and Elongation of Textile Fabrics." The model paintings and lining supports were cut into panels of 12" × 17" and 10" × 17" respectively. After lining, 1" wide samples were cut along the weft direction (in order to minimize extension of the crimp during peel testing).<sup>4</sup>

### *Model Painting:*

For the wax-resin tests, the model "painting" was linen, (Thread count: 19/18), with no ground. In preliminary tests with BEVA however, outside threads of the "painting" frayed during peel. As fraying could affect the measured peel strength, a linen with ground was used for BEVA tests. The linen was given two brush coats of Stevenson's acrylic gesso, slightly diluted. During ground application the canvas rested upon a rigid support to reduce penetration, since ground on the reverse has been found to affect the peel strength. One wax-resin sample was prepared with a ground for the purpose of comparison. (Sample designation: p2 ground).

### *Lining Supports and Pretreatments:*

Table 1 lists the fabrics tested as supports. Table 2 lists the two and three ply combinations tested. Table 3 lists the pretreatments that selected supports received. Further details on preparation of supports are given in Appendix 1.

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Table 1. Fabrics used as supports.

		Thread count (warp/weft)
Linen	Linen <i>Ulster # 9803</i>	18/19
Glass	Glass fibre <i>Burlington #7628</i>	23/17
<b>Polyester fabrics</b>		
p1	multifilament <i>Lincoln 578/65</i>	32/26
p2	multifilament <i>B. Henr. Lampe 2324</i>	23/19
p3	multifilament <i>B. Henr. Lampe 2325</i>	37/28
p4	multifilament <i>Terytex 1666</i>	24/23
p5	multifilament <i>Terytex 39</i>	18/22
p6	monofilament <i>Fyntx 60</i>	32/30
p7	monofilament <i>PeCap 80-177</i>	44/44
p8	monofilament <i>PeCap 7PE120-125</i>	62/62
p9	sailcloth <i>Hayward 00169/08Z</i>	30/62

Table 2. Combinations of fabrics and pretreatment for multilaminar supports.

Wax-resin linings	BEVA 371 linings
<b>2-ply supports</b>	
p1p1	p1p1
p1p1(R)	p1p1(R)
p2p2	p2p2
p3p9	p3p9
p1glass	p1glass
<b>3-ply supports</b>	
p1p8p1	p1p8p1
p2p8p2	p2p8p2
p3p8p3	p3p8p3

Table 3. Support pretreatments.

(B)	BEVA 371
(R)	acrylic <i>Rhoplex 234/Rhoplex 73</i> (1:1)
(P)	acrylic <i>Plexisol P550</i>
(A)	acrylic <i>Acryloid B72</i>

Lining, General:

Linings were undertaken according to procedures used by a conservator. The vacuum hot table (Convectron Mark II, Model I) was run at 6.8 kPa (2 in. Hg, 51mm Hg) with the “painting” face up. Sample preparation and lining were undertaken with as much consistency as possible, though some variations did occur. Linings were carried out in three batches for the wax-resin samples and nine batches for BEVA samples.

Wax-resin Lining:

A lining mixture of 8 parts refined Beeswax/1 part Multiwax W445/2 parts Laropal K 80 was brushed onto the prepared supports, except p9(B), and onto the model painting panels. Excess wax was removed during impregnation under vacuum. Lining followed as a separate procedure. When the wax flowed, between 63°–64°C (after 26 minutes), the samples were rubbed gently in both directions with a wad of soft felt. When the cooling fans were turned on after 31 minutes, final temperatures of 64°–66°C were measured at the hot table surface in a few locations.

BEVA 371 Lining:

Four panels of prepared lining supports were sprayed with BEVA all at one time; the samples were lined 24 hours later. BEVA was applied as consistently as possible by only one operator. Ten flocked coats of BEVA 371/VM&P Naphtha (1:1), warmed to 55°C, were spray applied using 276 kPa (40 psi) at the source and 110 kPa (8 psi) in the pressure cup. Samples were placed on the hot table in areas measured as providing the best temperature uniformity. The table was heated for approximately 31 minutes to reach a temperature of 70°C. The temperatures at the onset of cooling, measured at the hot table surface beside all samples, ranged from 78.5°–70.2°C.

Because BEVA is known to be affected by small differences in lining temperature and adhesive thickness a group of “repeat” samples (labelled “r”) were prepared

at a later date, being careful to duplicate the original preparation and lining procedures.

Weight differences between samples cut from the prepared supports and their average bare weight gave a range of weights of applied BEVA as  $13 \pm 4 \text{ g/m}^2$ .

#### Conditioning of Samples:

All lined samples were housed at ambient room conditions prior to testing ( $50\% \pm 8\% \text{ RH}$ ,  $21^\circ \pm 2^\circ \text{C}$ ). The tests reported in this paper were undertaken 4 years after lining.

#### Peel Tests:

Peel testing at  $180^\circ$  was undertaken on an Instron 4201 tensiometer, with a 50 N load cell. Three test specimens of each sample set were tested at a peel rate of 40 mm/min.

Peel tests were carried out both by peeling the lining support from the "painting," which is similar to actual practice when reversing a lining, and by peeling the "painting" from the lining support, which avoided the problem of peeling the lining supports of varying stiffnesses.

For the wax-resin tests, the environmental conditions were  $23^\circ\text{--}24.5^\circ \text{C}$  and  $46\%\text{--}58\% \text{ RH}$ . For the BEVA tests, conditions were  $23^\circ\text{--}24^\circ \text{C}$ ,  $46\%\text{--}53\% \text{ RH}$ .

#### Results and Discussion

For the samples in which the lining support was peeled away from the "painting," the peel strengths are given for wax-resin (fig.1) and for BEVA 371 (fig.2). Peel strengths in these figures are given in Newton/meter (N/m) on the lower scale and in kg/cm in the upper scale. Abbreviations in these figures are explained in Tables 1, 2 and 3. Repeat samples are labelled "r". For example, polyester (p1) samples had peel values around 160 N/m for wax-resin and 1400 N/m with BEVA 371.

#### Effect of Peel Configuration:

Two peel configurations were employed: peeling the lining support from the "painting" and vice-versa. The former configuration generally resulted in the adhesive bond failing at the adhesive/lining support interface. This resulted in the variety of strengths shown in figures 1 and 2.

Earlier tests were conducted in which the "painting" was peeled from the lining support. With the wax-resin samples, this peel configuration resulted in failure at the adhesive/ "painting" interface. As the type of lining support did not greatly affect the strength of this bond, the peel strengths were similar for all of the samples, i.e. about 550 N/m (fig.3). Therefore, although this method did avoid problems in peeling the lining fabrics of varying stiffnesses, it did not give very useful results for evaluating the various lining systems.

The results of the BEVA-lined samples were quite similar whichever configuration was used; the bond usually failed at the BEVA/"painting" interface. The bond between the flocked BEVA and the "painting" is designed to be weaker than the bond between the BEVA and lining material.

#### Peel Strength of Untreated Wax-resin Linings:

Wax-resin bond strengths varied between 715 N/m and 67 N/m depending mainly on the surface texture of the lining material.

The strongest bond strengths were produced with multifilament fabrics in which surface fibres were embedded into the molten wax. Microscopic examination of the peeled samples revealed that the wax-resin layer was disrupted by these fibres being pulled from within the layer. Multifilament fabrics with minimal "fuzz", e.g. Lincoln polyester (p1) had low bond strengths.

The smooth surface of monofilament threads provides little tooth for the wax-

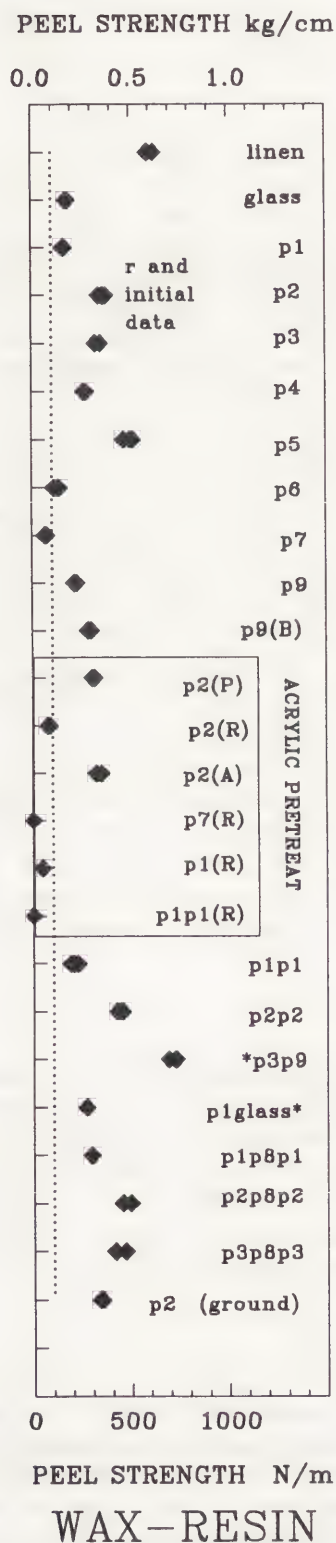


FIGURE 1 PEEL STRENGTH: WAX-RESIN (40mm/min peel rate; lining peeled from "painting"). 100 N/m is a general reference below which bonds are considered too weak. \* This side adhered to "painting". "r" Repeat sample.



PEEL STRENGTH kg/cm

0.0 0.5 1.0

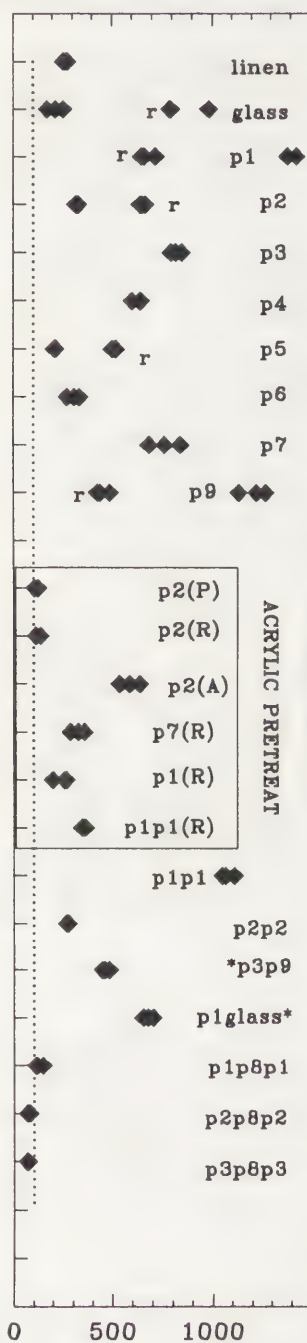


FIGURE 2 PEEL STRENGTH: BEVA 371 (40mm/min peel rate; lining peeled from "painting"). 100 N/m is a general reference below which bonds are considered too weak. \* This side adhered to "painting". "r" Repeat sample.

resin. The fabric embeds itself in the wax-resin but offers little adhesion. The higher bond strength of Fyntx 60 (p6) compared to PeCap 80-177 (p7) is due to the more open interstices between threads in the former fabric producing a coarser texture and more wax-to-wax adhesion through the lining support.

Fabrics with more surface texture, e.g. more crimp, produced higher bond strengths than those with smooth, even weaves. For example, Sailcloth (p9), which has a definite crimp in one direction, produces a stronger bond than the smooth, even weaves of Lincoln polyester (p1) and Glass Fibre. Similarly, the coarser weave of Lampe 2324 (p2) embeds itself more deeply into the wax than the more even weave of Lampe 2325 (p3).

#### Peel Strength of Untreated BEVA 371 Linings:

For the untreated single layer fabrics, the bond strengths ranged between 1476 N/m and 211 N/m. In contrast to the wax-resin samples, the results showed it is possible to have good adhesion between the monofilament fabrics and BEVA. As stated above, the bond failed at the BEVA/"painting" interface in most cases; however, there were areas of complete adhesive transfer to the "painting" (failure at the BEVA/lining support interface) in all samples having an average bond strength higher than 700 N/m.

There is a strong correlation between bond strength and the amount of embedding of the linen into the BEVA layer. Samples having high peel strength showed overall embedding (an overall imprint of the weave and linen fibres in the adhesive of the peeled sample), whereas samples having weak peel strength show minimal embedding.

Our method of lining with BEVA 371 gave inconsistent results, evident from the peel strengths of the repeat samples, (labelled "r" in figures 1 and 2). The repeat samples gave different results than corresponding earlier samples despite the fact that the preparation of both sets of samples was duplicated as closely as possible.

Conservators know by practice that temperature has a major effect on a BEVA bond. Studies by Hawker<sup>5</sup> and Pullen<sup>6</sup> have shown how sensitive BEVA is to lining activation temperature as well as adhesive thickness. Hawker also points out that time spent near the activation temperature, both heating and cooling, is important. This may explain the different results of the repeat samples. The increased embedding of the "painting" into the BEVA layer, which occurred in all samples of higher peel strength in the repeated pairs, may indicate differences in lining conditions; higher lining temperatures or longer time at the activation temperature occurred despite great efforts to ensure consistency.

The versatility of BEVA in producing a range of bond strengths is very useful; however, familiarity with one's own preparation and lining procedures is necessary to produce predictable results. Variations in temperature across the surface of the hot table could be problematic.

#### Effect of Pretreatment of Lining Support:

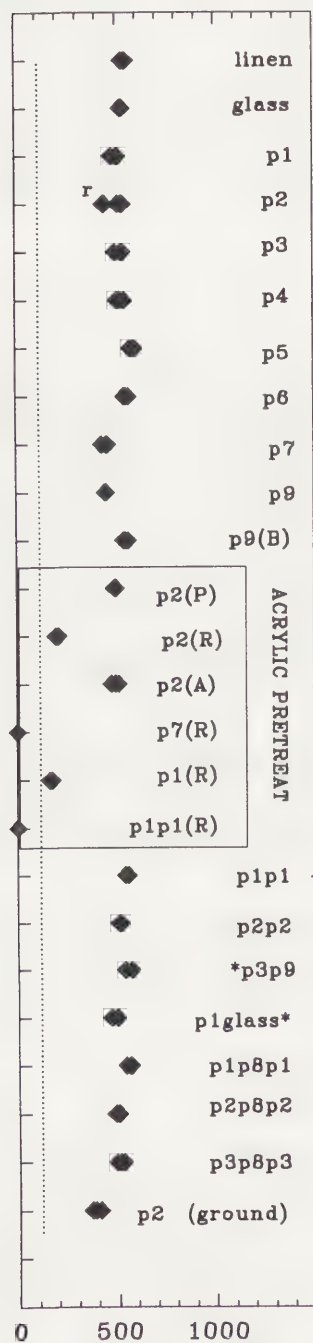
In this study, pretreatment in the form of "sizing" was undertaken in most cases to produce a stiffer, more isotropic lining support. The spray application of BEVA 371 to sailcloth, p9(B) was intended to improve the wax-resin bond which it did slightly.

The wax-resin linings with Rhoplex pretreatment resulted in very low bond strengths (0 to 80 N/m), which were considered too weak to be acceptable. The Rhoplex application almost entirely filled the weave texture of the lining fabrics producing a slick bonding surface. Plexisol P550 and Acryloid B72 pretreatments with the wax-resin lining had no clear effect on peel strength. The Plexisol P550 and B72 treatments altered the "stiffness" and "feel" of the fabrics but did not fill the weave texture at the bonding surface.

For the BEVA samples, because of the inconsistency in the results, it is difficult to draw conclusions about the effect of the pretreatments. The slick Rhoplex saturated surfaces did however, appear to affect the bond between the Beva and

PEEL STRENGTH kg/cm

0.0 0.5 1.0



PEEL STRENGTH N/m

WAX-RESIN

FIGURE 3 PEEL STRENGTH:  
WAX-RESIN (40mm/min peel rate;  
"painting" peeled from lining). 100  
N/m is a general reference below  
which bonds are considered too weak.  
\* This side adhered to "painting".  
"r" Repeat sample.

the lining support, as some failure (adhesive transfer) at this interface was observed in samples with peel strengths as low as 240 N/m.

#### *Effect of Lining Support and Thickness:*

In the case of wax-resin lining, all untreated laminates had higher bond strengths than their single layer counterparts, for example, p1 and p2 compared to p1p8p1 and p2p8p2 respectively. The stronger bonds of the thicker supports may be related to the peel angle and the thickness of the lining support.<sup>7</sup> The curvature of the lining support during peel is larger for the thicker laminated lining supports, which appears to result in the peel occurring over a wider interface than the thread to thread release of the thin supports. The bond strengths of single layer supports may also be affected by thickness; for example, Terytex 39 (p5) compared to Terytex 1666 (p4).

In the case of BEVA lining, the addition of a third layer to the laminate caused a significant decrease in the peel strength because an adequate temperature was not reached at the lining interface during the lining procedure. This confirms that the temperature should be monitored at the level of the lining adhesive on the hot table.

#### *Effect of Rate of Peel:*

Peel rate will affect the measured peel strength and so must be considered when comparing results. Peel tests were conducted at CCI at two peel rates, 2mm/min and 40mm/min.<sup>8</sup> As expected, the slow peel wax-resin strengths were consistently weaker than the fast peel, giving an average ratio of 61% ± 10%.

It has been argued that a slow peel rate has the advantage of being more similar to the stresses that may cause delamination in a lined painting. The slow rate however, still does not reproduce the effect of years of stress on a lining and therefore shows no clear advantage over the faster rate. The faster peel rate allows more samples to be peeled within a reasonable time period, resulting in better statistical precision.

#### *Effect of Ageing:*

It has been reported that the peel strength of some lining adhesives changes with time.<sup>9</sup> In this study, some samples were peeled, then peeled further 2 weeks and 1–2 months after lining; others were peeled at 2 weeks and 4 years after lining.<sup>10</sup> Additional samples cut from the original sample panels were peeled four years after lining. No clear trends indicating a significant increase or decrease in strength were found for either adhesive.

#### *Estimation of "Adequate" Bond Strength:*

No one has objectively established the strength needed to resist delamination under normal environmental stresses. Phenix and Hedley<sup>11</sup> chose 115 N/m (2mm/min peel rate) as a minimum working requirement for a lining adhesive bond. Three conservators at CCI hand-tested the peel of various BEVA samples. Samples around 100 N/m (2mm/min peel rate) were thought to be weak. Similarly Katz comments that even though his BEVA 371 lined samples had peel strengths just below or around 115 N/m they still produced a strong enough bond for the intended "nap" bond lining (2mm/min peel rate).<sup>12</sup>

Thus, various researchers generally agree on a minimum "acceptable" bond strength: about 100N/m.<sup>13</sup> What is too strong may be dependent on the lining fabric. In the CCI ratings, for example, glass fibre lined with BEVA, 558 N/m at 2mm/min peel rate, tore during peeling, whereas 565 N/m at the same peel rate was considered only as "strong" for the sailcloth sample. Of course, the suitability of a bond within the acceptable range is dependent upon the painting being treated.

The failure of real linings can also give useful information if the lining materials and procedures are well-documented. The authors would be interested in hearing of instances of delamination with these or other lining systems.



### Conclusions

1. The peel strength of the wax-resin samples depended mainly on the surface texture of the lining support. Peel configuration has a major effect on the testing of wax-resin lined samples; joint failure predominantly occurs between the adhesive and the substrate which is peeled away.
2. Lining with BEVA 371 can result in a wide range of bond strengths. While this can be an advantage for a conservator, it is also difficult to control. Replicate samples that were fabricated on different days had very different strengths, despite efforts to be consistent in the application of adhesive, lining temperature and duration of the lining process.
3. Pre-treatment of the lining support with Rhoplex 234/73 (1:1) resulted in a lower bond strength for wax-resin samples, due to decreased adhesion between the slick Rhoplex-saturated surface of the lining support and the lining adhesives.
4. Factors such as peel rate, type and thickness of lining support, adhesive coat weight, method of application and lining conditions can have a large effect on the measured peel strength. Some reported differences in peel strength may not be due to a difference in bond strength between samples, but to these other factors. Peel tests are useful for ranking samples if all parameters are held constant, but useful comparison of results from different researchers is difficult.
5. Peel tests may be useful in providing guidelines for the refinement or design of lining procedures, but it is important that conservators test mock-ups of new procedures in their own laboratory before deciding a lining system is adequate.

### Acknowledgements

The authors wish to thank and acknowledge Charlie Costain for writing the peel strength programs, for his guidance on the use of the Instron machine and for his assistance with the analysis of the results.

### Materials

Linen #9803: Ulster Weaving Co., Ltd., 148 Madison Ave., New York, N.Y., 10016, (212) 684-5534

Glass Fabric #7628: Burlington Glass Fabrics Co., 1345 Avenue of the Americas, New York, N.Y., (212) 333-7323

Polyester 578/65: Lincoln Fabrics, 63 Lakeport Rd., St. Catharines, Ontario, L2N 4P6 (416) 934-3391

Polyester 2324; 2325: B. Henr. Lampe. B.V., Julianstraat - Sophiastraat, Postbus 202, 8600 AE Sneek, Holland, 05150-1 25 41

Terytex 39; 1666: P & S Filtration Inc., Jordan Rd., Skaneateles Falls, New York, 13153, (315) 685-3466

Fyntx 60; Polyester PeCap 80-177: B & SH Thompson Co. Ltd., 8148 Devonshire Rd., Town of Mount Royal, Quebec, H4P 2K3, (514) 739-1971

Sailcloth (unimpregnated); Picture Restoration Fabric; 00169/Z: Richard Hayward & Co., Tiverton, Devon EX16 5LL, England (0884) 257867, FAX 252866

BEVA(R) 371; ethylene/vinyl acetate copolymer (major ingredient): Conservator's Products Co. of Canada, 23 Morrow Ave., Toronto, Ontario, M6R 2H9

Laropal K 80; polycyclohexanone resin: BASF, P.O. Box 430, Stat. St. Laurent, Montreal, Quebec, H4L 4V8 (514) 341-5411

Multiwax W445; microcrystalline wax: Witco Chemical Co., S1200-2 Lansing Square, Willowdale, Ontario, M2J 4Z4

Rhoplex 234, Rhoplex 73; Methyl methacrylate/ethyl acrylate copolymer emulsions; Acryloid B72; Ethyl methacrylate/methyl acrylate copolymer: Rohm & Haas Canada Ltd., 2 Manse Rd., West Hill, Ontario, M1E 3T9 (416) 284-4711

Plexisol P550; Butyl methacrylate (40% in petroleum ether): Röhm GMBH Chemische Fabrik, D-6100 Darmstadt, Postfach 4166, Germany

Stevenson's Acrylic Gesso; Titanium white and acrylic emulsion: David L. Stevenson & Son, Toronto, Ontario

### Notes

1. D. Daly and S. Michalski, "Methodology and Status of the Lining Project, CCI", *Preprints of the 8th Triennial Meeting of the ICOM Committee for Conservation*, Sydney, (1987), vol.1, pp. 145-152.
2. Previous peel tests investigated: 1) the influence of warp/weft and bias cut samples on peel strength; 2) the influence of 22 wax-resin mixtures on peel strength; and 3) the same samples used in this study using a different peel configuration (peeling the "painting" from the lining support) at two rates of peel, (2mm/min and 40 mm/min), and in some cases, peeling at different times after lining. Results are available from Debra Daly Hartin.
3. A. Phenix and G. Hedley, "Lining Without Heat or Moisture", *Preprints of the 7th Triennial Meeting of the ICOM Committee for Conservation*, Copenhagen, (1984), p.38.
4. In an earlier study, the peel strength of samples in which the linen was cut along the warp or bias, varied only slightly. The peel strength of weft cut samples was significantly higher; an average of 24% higher for the three lining supports tested. Weft cut samples did not deform as much during peel and were easier to cut.
5. J. J. Hawker, "The Bond Strengths of Two Hot Table Lining Adhesives—Beva 371 and Plextol D360", *Preprints of the 8th Triennial Meeting of the ICOM Committee for Conservation*, Sydney, (1987), pp. 161-168.
6. S.P. Pullen, "The Effect of Variables on the Bond Strength of Beva 371 Linings", (Report for the degree of Master in Art Conservation), Queen's University, (1991).
7. A.J. Kinloch, *Adhesion and Adhesives*, Chapman and Hall, New York, 1990, pp. 302-306.
8. See Endnote 2.
9. J.J. Hawker, "The Bond Strengths of Two Hot Table Lining Adhesives—Beva 371 and Plextol D360", p. 164. Phenix and Hedley, "Lining Without Heat or Moisture", p. 42.
10. See Endnote 2.
11. Phenix and Hedley, "Lining Without Heat or Moisture."
12. Katz, "The Quantitative Testing and Comparisons of Peel and Lap/Shear for Lascaux 360 H.V. and Beva 371", p. 67.
13. As the value of 100 N/m is subjective, we are applying it to the results of both our 40mm/min peels and our 2mm/min peels.

### Appendix 1. Description of pretreatments and laminate preparation.

	Wax-resin lining	BEVA 371 lining
p9(B)	4 spray coats of BEVA 371 onto sailcloth; lined onto wax impregnated linen.	
p2(P)	10% Plexisol P550/Mineral Spirits brushed on fabric until saturated.	
p2(R)	Rhoplex 234 + Rhoplex 73 (1:1) brushed on fabric until saturated, squeegeed to even.	
p2(A)	10% B72 in xylene brushed on both sides of fabric, squeegeed to even.	
p7(R)	Same as p2(R).	
p1(R)	Same as p2(R).	
p1p1(R)	Rhoplex 234 + Rhoplex 73 (1:1) brushed on laminate until saturated, squeegeed to even.	
p1 glass	Fabrics placed together layered structure, wax-resin applied by brush and laminated on hot table.	Layers placed together and brushed (to provide translucency) with BEVA 371/VM&P Naphtha (1:1) until saturated, squeegeed to even.
2-ply supports	Fabrics placed together layered structure, wax-resin applied by brush and laminated on hot table.	BEVA 371 sprayed onto both inner sides and laminated on hot table.
3-ply supports	Fabrics placed together layered structure, wax-resin applied by brush and laminated on hot table.	BEVA 371 sprayed onto both sides of inside layer and laminated on hot table.



### Abstract

The technique and state of preservation of a group of traditional painted wall hangings is presented. The paintings have dual importance as objects of art and bearers of cultural and historical information. Earlier conservation treatments have often disregarded their intended character and the way they were used. A new method for treating porous and flaking layers of glue paint on flexible textile supports is outlined. The method enables treatment without disturbing the original appearance of texture and gloss, or the textile character of the painting. Employing a suction table, the treatment includes moisture softening and consolidation of the paint layers using sturgeons glue, as well as lining of the textile support using Plextol D360 and Hollytex 3257 polyester fabric.

### Keywords

Conservation, glue, tempera, paintings, textile, flaking, moisture, humidification, lining, suction table

## The Study and Conservation of Glue Paintings on Textile: 18th and 19th Century Painted Wall Hangings from Southern Sweden

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### Introduction

The painting of wall hangings *bonader* as it occurs in the 18–19th centuries in southern Sweden derives from old traditions (1). Archival sources provide evidence that painted wall decorations on woven fabric have occurred all over Scandinavia and were part of church furnishings from the early Middle Ages and throughout the Renaissance. Decorative paintings directly on the walls or on woven fabric flourished early in the upper classes. This custom was eventually taken over by the peasant population (2).

Swedish painted hangings which still exist are concentrated in three geographical areas. The oldest ones, from the end of the seventeenth century, come from the northern region of Hälsingland and Gästrikland. During the middle of the eighteenth century, the painting of wall hangings developed in the southern regions Småland, Halland, Skåne and Blekinge, where the custom eventually seems to have penetrated the whole farming and middle class societies and left the greatest number until the present time (3). The paintings of the third region of Dalarna (Dalecarlia) are of a somewhat later date. They have generally been more well-known and it is not unusual for paintings from other regions to be called "Dalarna paintings".

Craft products are often strongly shaped by the form of the dwelling, the hearth and the furniture. Still in the mid-eighteenth century many of the farmhouses

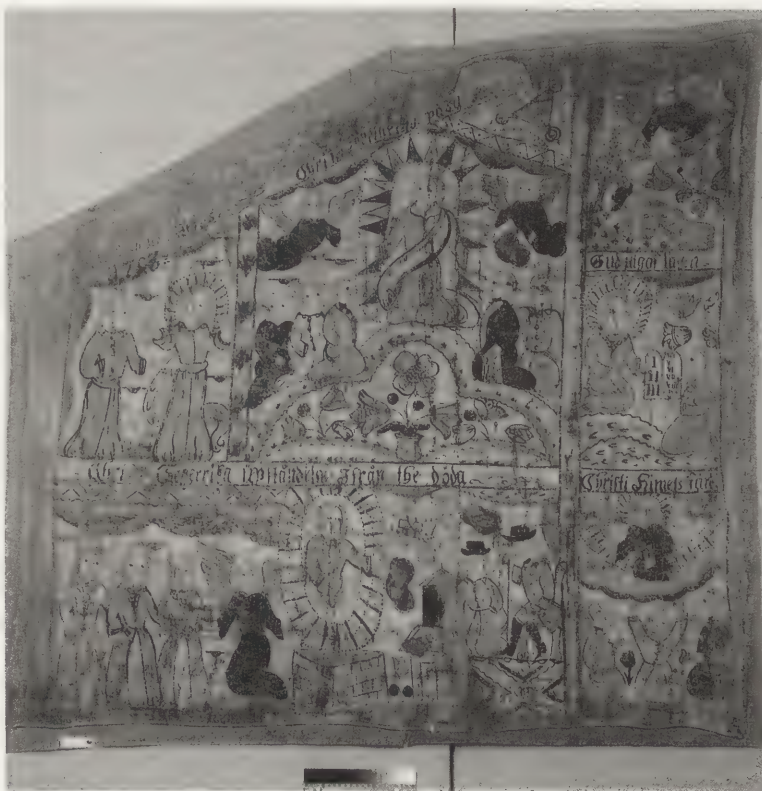


Figure 1. Painted hanging on textile, fitted to a gable wall, depicting from left to right: Christ and Nicodemus, The Transfiguration of Christ, The Resurrection of Christ, Elijah in the Desert, Moses receiving the two Tablets of the Testimony and The Ascension to Heaven. Dated 1783. Attributed to Per Nilsson, Ljushult. Göteborg: Historiska Museum, GM Allm 3218, 126 × 136 cm.

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Figure 2. Painted wall hanging on textile with printed wall paper along the lower edge.

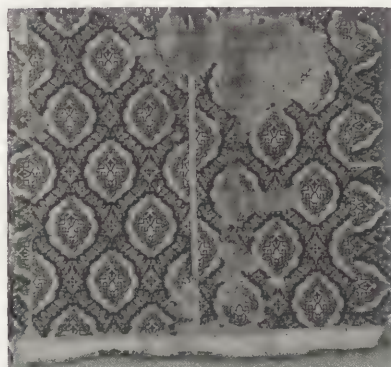


Figure 3. Back of painting shown in Figure 2.

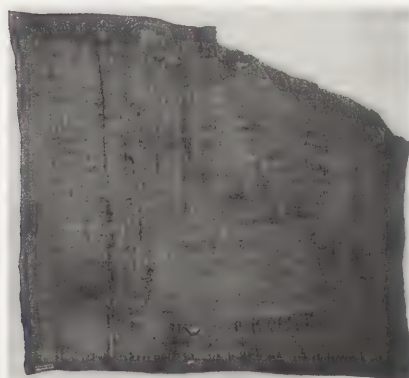


Figure 4. Back of painting shown in Figure 1.

Table 1. Pigments.

Blue:	Indigo, Prussian Blue, Ultramarine Blue
Red:	Red Iron Oxide, Red Lead, Vermilion, Brazil-wood Lake
Yellow:	Yellow Ochre, Lead pigments, Lakes of Birchleaves and other yellow vegetable dyes
Green:	Mixed blue and yellow, Verdigris, Arsenic greens
Brown:	Ochres, Umbers, Van Dyke Brown
Black:	Lampblack, Charcoal
White:	Whiting, Lead White

in southern Sweden did not possess a chimney. The smoke escaped through an opening in the ceiling, encrusting the walls and ceiling with soot, making any permanent decoration of the room futile. At holidays, especially at Christmas, the houses were lined with hangings of various sizes and shapes, carefully fitted to the sloping ceiling, the gables and the low walls above the permanent benches, and pinned directly onto the logs (see Figure 1). Thus the trimmed interior did present a tentlike appearance. After the feast the hangings were taken down, rolled or folded up and stored in wooden chests together with other textiles.

The custom of detachable wall decorations persisted in the region for a century from around 1750 (4). From the beginning of the 19th century the paintings were often executed on paper instead of textile. When printed wallpaper became available to ordinary people, the wall hangings went out of fashion. In many cases they were left on the wall for insulation under the more fashionable wallpapers (see Figures 2 and 3).

The motifs are mostly religious, taken from Bible illustrations and engravings. However, the costumes and setting of the figures in the painting belong to the painter's own time. The pictorial scene is always accompanied by one or more horizontal bands of text in block letters, usually a quotation from the Bible, giving a reference to the text cited and the year of the painting. Only a minority of the paintings are signed, but in many cases the hand of the painter is easily recognized. The painters were, at least in the beginning of the period, not professional artists but rather part time painters wandering around in their home districts painting on orders from the more wealthy farmers.

#### Materials and technique of the paintings

The woven linen fabric was usually supplied by the customer, and its quality and condition vary greatly. Often pieces of available used and mended household linen in tabby or twill, such as bedsheets, sacks or shirts were sewn together to fit a precise wall space (see Figure 4). Worn wall runners with inlaid patterns and fringes were not infrequently used as support. Only in rare cases new or whole pieces of linen cloth have been used. The final paintings are usually between 0.25 and 1 m wide and often more than 4 m long. Before the paint was applied, the textile was stretched, pinned flat to the wall, and treated with a wash of animal glue.

The ground consists of whiting mixed with animal glue. Cross sections show that the ground has been applied in one or more layers depending on the texture of the support and the intended surface character of the final painting. The ground is usually integrated as background in the composition. In cases, where the surface of the painting is glossy, the ground has been treated with a final priming of glue before the paint has been applied. In some cases a small amount of pigment, usually yellow ochre and/or charcoal black, has been added, to tint the otherwise white background. Paintings with a matt surface usually have a very thin ground without priming. When the background is tinted the pigments have been mixed with the ground.

In written records, or more often by oral tradition, the medium in the early paintings is said to be tempera made from products available in the household, such as egg, milk and home-cooked polysaccharide pastes (1, 5, 6). The same sources also mention that animal glue has been produced by the painters themselves or supplied by the customer. Preliminary tests, specific for the amino acid hydroxyproline in collagen show that animal glue has been the principal medium in all paintings tested so far in our laboratory (7). No attempts have been made to demonstrate the presence of egg or casein.

The pigments used were bought from the local store or prepared by the painters themselves (1, 5) (see Table 1). The palette of the early painters is more restricted than in later periods, with a tone similar to the romanesque wall paintings in the churches. Later the colours are usually brighter and more intense. Some of the organic pigments, in particular Brazil-wood, have sometimes been used as glazes with a high content of glue. The surface appearance is characteristic for the technique of the painter. The paintings have never been varnished.





Figure 5. Detail of the back of the textile support showing accumulated dirt.

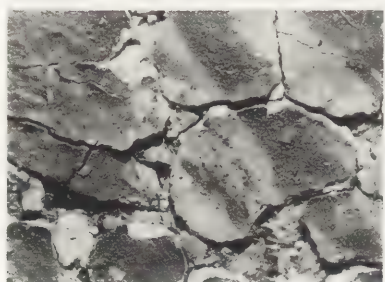


Figure 6. Detail showing cracking and flaking of the ground and paint layer.



Figure 7. Painted hanging shown in Figure 1 in raking light.

### Condition

A survey of the condition of 292 painted wall hangings on textile has been performed (6). Much of the damage that the wall hangings present today has been caused by the fact that their materials and technique are incompatible with the handling and temporary display they have experienced. The problem is obvious with the very long and unwieldy paintings. However all of them have been repeatedly pinned up, taken down and folded during their "active" lifetime. The linen fabric, which in many of the paintings was worn and mended already from the beginning, has tears and broken stitches caused by mechanical stress. In addition there has been chemical deterioration of the cellulose fibres, partly due to microbial activity during storage in damp and closed chests. Dirt and later added material have contributed to the damage (see Figure 5). Along the edges iron nails have caused tears and rust stains and sometimes considerable loss of fabric. The mechanical breakdown, together with the structural weakness of the fabric, means that the textile no longer can carry its own weight.

The ground and paint layers usually show considerable cracking and flaking (see Figure 6), primarily due to strain from movement of the support and mechanical wear, but also due to loss of adhesion between the support and the ground as a consequence of humidity and microbial activity. Paintings with a matt surface often have very porous and powdery paint layers. In areas with red organic pigment or carbon blacks there is extensive cupping due to a high vehicle/pigment ratio. There are also disfiguring water stains resulting from the diffusion of deterioration products from the support and glue. Surface dirt, soot and sometimes remnants of printed wall paper and glue paste make the colours obscure. Poor light-fastness of the organic pigments has changed the mixed greens to a greyish-blue and the Brazil-wood red has often faded completely.

Inappropriate storage facilities and display in the museums as well as improper or incomplete conservation and restoration treatments have accelerated deterioration or changed the original character of the paintings.

### Earlier conservation treatments

Concerning conservation of painted wall hangings in the past, it has been unclear whether to regard them as textile objects or paintings. The treatment has therefore depended on the special skills of the local conservator (6).

Textile conservators have mostly concentrated their efforts on supporting the linen fabric according to traditional methods, with numerous stitches and patches of new linen cloth, leaving the ground and paint layers without treatment. In many cases the paintings have been sewn onto a whole new canvas. The result of this textile conservation is a well preserved textile support but a continuous flaking of the ground and paint layers (see Figure 7).

Painting conservators have generally used conventional methods for paintings on canvas, including lining on a new linen canvas with glue-paste, mounting on a stretcher and framing. In this way the ground and paint layers as well as the linen support are no doubt protected from mechanical deterioration, but the original character of the hanging is completely lost and the risk of chemical deterioration has increased. The treatment has often included extensive inpainting of the figures and of missing text and dating.

### New approach to conservation of painted wall hangings

For a category of objects which does not naturally fall into a well defined group of objects, it is essential to describe their specific elements and character before any treatment is decided upon.

The importance of the painted wall hangings is dual. They not only possess a certain artistic and decorative value but also are important bearers of historical and cultural information. The character of a detachable, loosely hanging textile must be considered at the same time as the necessity to secure the porous and flaking paint layers. The surface appearance and texture are characteristic for the technique of the painting. The choice of consolidation medium for the paint



layers must leave the original texture intact. Filling in of missing ground or inpainting is kept to a minimum.

### Cleaning

The entire painting is very hygroscopic and thus strongly affected by water. Attempts to treat water stains and other disfiguring spots in the paint layers with water on the suction table have not been successful. In some cases they have even enhanced the damage by transporting pigments down into the ground layer. Tests with non-polar and polar solvents have also failed (6). Thus, dry methods have been the only way to proceed. This includes careful vacuum-cleaning and mechanical removal of surface dirt and deposits with a brush or a scalpel.

### Humidification and consolidation of the paint layers

Treatment with moisture together with low heat under pressure seems to reactivate the medium and brings about an optical change in the porous paint layers such that the colours become more clear. Moisture treatment alone also seems to increase the stability of the deteriorated linen fibres. The visibly positive effect is usually only temporary and reversible unless new binding medium is added. The amount of medium needed is usually small. The primary concern is how to make the added medium penetrate into the whole depth of the porous and fibrous material, such that a satisfactory consolidation is attained, without displacement of the pigments, change of the surface texture, or alteration of the flexibility of the painted hanging.

A series of tests with solutions of cellulose ethers, acrylic resins and collagen glues have been performed earlier in our laboratory, with respect to consolidation of glue paint (6, 7). The best results were achieved with sturgeons glue and gelatin. An aqueous solution of sturgeons glue has the advantage of a lower surface tension than gelatin and can therefore be expected to wet and penetrate the material more easily. A moderate heat will decrease the viscosity and enhance the flow of the solution, such that the penetration, before setting of the glue, is increased.

### Treatment procedure

After mechanical cleaning the painting is placed upside-down onto a suction table, which has been covered with a porous non-absorbent membrane and on top of that a film of Vilene, a non-woven polyester/cellulose fabric (Freudenberg). An aerosol of water is sprayed over the linen fabric, enough to make it damp but not wet. Then a film of Melinex is placed on top of the humidified painting to create a closed humidity chamber. The heat is turned on and the temperature is allowed to rise to around 35°C. Then the Melinex film is removed, and the back of the painting is treated with an aerosol of 1.5–2 % sturgeons glue in water. The amount of glue added depends on the thickness of the paint layer and textile and the need of binding medium. The textile is clearly damp and slightly sticky but not really wet. The painting is then turned over (front up), and the paint layer is sprayed with a small amount of 1.5 % sturgeons glue. Now the painting is covered with a film of Vilene and on top of that a film of Melinex (see Figure 8). The heat is turned off. When the temperature has fallen to around 25°C (ca 30 minutes) the pressure is turned on and kept at 50 bar until the painting is dry. The use of a non-absorbent membrane under the painting, instead of a blotting paper, decreases the drying time considerably. The polyester/cellulose film protects the damp paint layer from becoming glossy in contact with the Melinex, when under pressure, and it does not stick to the sturgeons glue.

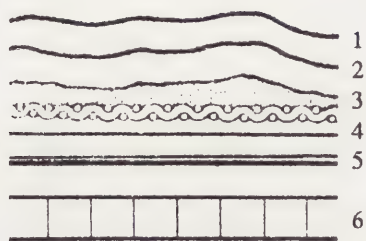


Figure 8. Schematic representation of the consolidation treatment on the suction-table: 1 = Melinex, 2 = Vilene, 3 = painting, 4 = Vilene, 5 = porous non-absorbent membrane and 6 = perforated aluminum sheet.

### Lining

The lining fabric is an ordinary linen canvas with a quality and natural colour chosen to match the textile in the painting. The linen canvas is rinsed twice in hot water in a large wash basin in the textile conservation work shop. The



canvas is dried flat on an even surface and allowed to shrink without being stretched. In this way the canvas is expected to adapt to possible movements of the textile fibres in the painting, when it is exposed to changes in the relative humidity. The painting is laminated, on the suction table, onto a new linen canvas with an interleaf of Hollytex 3257, a non-woven polyester fabric (Lascaux), impregnated with Plextol D360, a thermoplastic acrylic resin (Röhm). The edges of the lining canvas are turned to the back and fastened with the same type of interleaf as used in the lining.

### Mounting

In attempts to imitate the original hanging of the paintings three different methods have been tested: - 1. a sleeve along the upper edge of the lining canvas, designed to take a rectangular-profile aluminum batten; - 2. Velcro (R) along the upper edge, and - 3. metal eyelets along the upper edge and sometimes along all edges of the lining canvas. The third method allows a very narrow upper edge and is the least visually disturbing arrangement.

### Storage

The preferred storage for the painted hangings is on a flat surface. For the often very large objects an acceptable compromise is to roll them around cardboard rollers, 25 cm in diameter, with an interleaving cloth of unbleached cotton (see Figure 9).

### Conclusion

So far 18 painted wall hangings on textile have been treated at our workshop according to the general principles described. Our aim has been to keep the intervention at a minimum in order to retain the integrity of the object. This has been possible by using a carefully controlled humidification technique and a minimal amount of consolidation medium innate to the painting. The use of a suction table creates an even pressure conditioned to restore contact within the fibrous support and the porous paint layers. The treatment is possible to control even with very large formats which may have to be treated in sections. The main drawback of the process is that which goes with all lining treatments, i.e. that every irregularity of the support becomes visible, and that the back of the painting is hidden.

### Materials

Gelatin (powder), 1.1933. KEBO Lab AB, S-163 94, Telephone 08-7600020, Fax 08-7605794.

Porous non-absorbent membrane, non-woven polyester fabric, ca 2 mm thick (Schabrackenvlies 64202). Vereinigte Filzfabriken AG, 7928 Giengen/Brenz, Telephone (07322) 144, Fax (07322) 144-246.

Vilene 105, non-woven polyester/cellulose (60/40) fabric. Carl Freudenberg, Postfach 10 03 60, D-6940 Weinheim (Bergstrasse).

Hollytex 3257, non-woven polyester fabric. Lascaux Restauro, Alois K. Diethelm AG, CH-8306 Brüttisellen, Telephone 01-8330786, Fax 01-8336180.

Plextol D360, thermoplastic acrylic resin. Röhm GmbH, Postfach 4242, Kirchschallée, D-6100 Darmstadt 1, Telephone (06151) 8061, Fax 6151-184233.

Velcro (R), Duetto, polyamide. Tessitura Luigi Ortalli Laurent, Baranzate di Bollate (Mi) 20021, Via 1aa Maggio, 45, Italy, Telephone 3-561-440/45, Fax 3563696.

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Figure 9. Painted wall hangings rolled around cardboard rollers with an interleaving cotton cloth.

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### Abstract

Though many similarities exist in the use and effects of solvents and resin soaps when used to clean paintings, there also are many differences. The mechanism of cleaning by resin soaps includes detergent action, alkaline extraction of acidic compounds, and swelling and solvation by solvent components. In some cases, the components of resin soaps contribute enough solvent activity to the soap mixture to blur these differences. Nevertheless, enough differences exist that the criteria used to judge the success of solvent treatments may be misleading when used to evaluate resin soap treatments. More work is required to determine appropriate criteria with which to judge such treatments. One of the major differences between solvents and resin soaps is the presence in soap mixtures of nonvolatile materials that leave residues. Both the short- and long-term effects of these materials require more study. Until the results of such studies are available, resin soaps should be carefully formulated in order to minimize potential problems.

### Keywords

Paintings, cleaning, resin soaps, solvents

## Resin Soaps and Solvents in the Cleaning of Paintings: Similarities and Differences

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### Introduction

Cleaning is a critical process in the conservation of paintings. Organic solvents are the tools most widely used for the removal of dirt, overpaint, and varnish. The long history of the use of solvents, as well as research into their actions in the cleaning of paint films, has resulted in a large body of practical, experimental, and theoretical knowledge. Solvents are not ideal for use in every situation, however, and various other methods of cleaning paintings have been employed. These methods include the use of alkalis, mechanical action, enzymes, gels, and surfactants. Recently, a system of aqueous cleaning mixtures, including resin soaps, has been introduced (1). Depending on the treatment situation and the approach of the conservator, resin soaps can be considered either as a secondary choice when no satisfactory solvent system can be found, or as the method of first choice. In either case, the approach and goal for each technique (solvent or resin soap cleaning) is the same: to find a mixture that when properly applied will help to remove unwanted materials and layers and leave the original layer intact and unaffected to the extent possible. Resin soaps often are applied and handled in a manner similar to solvents, are modified to optimize their cleaning action much the same way as solvent mixtures are adjusted, and may include solvents as important components. This similarity often also extends to the way the results of cleaning with resin soaps are evaluated, even though their ingredients, effects, advantages, disadvantages, and proposed mechanism of action are very different. This paper is a discussion of those differences and their implications.

### Solvent action

Solvents interact with materials by forming a homogeneous mixture. Small molecules can be dissolved in an appropriate solvent (dissolving a varnish), while materials containing large insoluble molecules, such as a crosslinked polymer, will only be swollen by the spread of a solvent through it. Often, swelling alone will soften a material enough that it can be dispersed and removed mechanically. Both processes can occur in a non-homogeneous material such as a dried oil film, with the solvent both swelling the crosslinked oil matrix and extracting out small molecules into solution. The word "dissolve" implies going into solution with no permanent chemical change; thus, a solute can be recovered by either precipitation or evaporation of the solvent. For instance, strong alkali is not a true "solvent" for oil films, because the alkali chemically disintegrates the oil in order to disperse it. Most liquids considered as solvents are relatively inert; while they interact with a substrate, they do not react with it. This does not mean that no change occurs since, for instance, polar solvents such as alcohols and water can disrupt oil-pigment bonds (2). Most of these interactions are relatively well understood and can be quantified in terms of solvent parameters (2).

A material such as a dried oil film can also be characterized in terms of the degree to which it is affected by solvents covering the range of solvent param-

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eters. If the solvent parameters of a solvent that has *not* been tested on an oil film are known, its effects on an oil film relative to those of solvents that *have* been tested can be predicted fairly accurately.

Most liquids considered for use as solvents are volatile and will eventually evaporate completely. Though changes caused by solvents may influence the subsequent permanence of oil films, these changes are essentially complete by the time that the solvent evaporates.

The combination of relative inertness, predictable short-term behavior, and a lack of continuing effects after they evaporate means that new solvents can be introduced for use in cleaning with a minimum of testing.

One of the motivations for the introduction of new solvents is concern about the volatility and toxicity of some solvents which have been used. The use of less toxic or less volatile alternatives, either other solvents or other cleaning reagents, is desirable for health reasons.

### **Detergent action**

Detergents and soaps function by dispersing clusters of material throughout an aqueous system (3). Soap molecules can form these micelles because they have both a polar and non-polar segment. Groups of solvent molecules form a shell around a cluster of an otherwise water-insoluble material. The non-polar end of each soap molecule orients toward the center of the cluster of low polarity material, while the polar end faces outward to provide a water-soluble outer surface for the micelle. Individual soap molecules are generally larger than solvent molecules and do not penetrate solids well. Even if soap molecules penetrate a solid material, they cannot function individually to form micelles. Some mechanism other than detergent action is required to break up the material to be dissolved to form the micelles. This may be achieved by mechanical agitation (swabbing), by the swelling action of a solvent added to the mixture, or by the alkalinity of a soap mixture resulting in the solubilization of acidic compounds in the material or partial hydrolysis of a material such as a dried oil film. The cleaning action of soap mixtures thus may combine many processes, including solvent action, in various proportions.

The complexity of resin soap mixtures and their cleaning action as compared to dissolution or swelling by solvents means that the effects of the resin soap mixtures are less predictable. One has to consider parameters relating to both the polar and non-polar portions of the soap, the minimum concentration required before the soap will form a micelle, the pH of the mixture, and the function of any other materials added to modify the action of the mixture. Resin soap mixtures are generally less hazardous to health, for two reasons. First, most of a resin soap mixture is water. Soaps can be effective at relatively low concentrations, usually less than ten percent. Second, most of the non-water components of resin soap mixtures are nonvolatile, meaning that hazardous vapors are reduced or eliminated. The complex mode of action and inclusion of non-volatile components makes the use and effects of resin soaps very different from that of solvents.

### **Residues**

During the process of cleaning a varnish or paint film with solvents, some solvent is always left behind. The penetration of a solvent into a material produces a concentration gradient, with a high solvent concentration at the surface and a low concentration of solvent at the solvent front. At the surface, the solvent concentration is sufficiently high to dissolve or soften the material so that it can be removed mechanically. At some point below the surface, however, there is not enough solvent to render the material removable (2). Any solvent below this level will be left behind after cleaning. The residual solvent has several effects, such as making the material softer and deepening or saturating the color. The extent of these effects is directly related to the amount of solvent present, and will be reduced and largely reversed as the residual solvent diffuses to the surface and evaporates. Some changes, such as a hardening of the material



due to the extraction of low molecular weight components, may be permanent, but the solvent itself can cause no further changes once it has evaporated.

The inclusion of nonvolatile materials in resin soap mixtures immediately raises the possibility that not all of the nonvolatile components will be removed during the cleaning process. Being nonvolatile, they would not evaporate and would remain in or on the paint film. Such residues might be difficult or impossible to remove without affecting the paint film. Two concerns arise from the presence of residues. The first is that the presence of nonvolatile materials might affect the optical properties of the paint film. The visual appearance of a paint film is due largely to its surface characteristics, and very small amounts of material in or on the surface can produce visible effects. The second concern is that the residues might not be inert and would remain active. The concentration of the nonvolatile components of the resin soap mixtures increases as the water evaporates. However, the mixture does not necessarily evaporate and leave an inert solid, since some common components of resin soap mixtures are liquid or hygroscopic (retaining water).

Residues have, in fact, been found by those researchers who looked for them (4-6). These investigations have focused on residues of the soap itself, but there is also evidence that a common nonvolatile liquid ingredient of resin soap mixtures, triethanolamine, is absorbed by paint films (7).

### **Effects of resin soaps and solvents on paint films**

Solvents can have a number of undesirable effects on paint films. These effects include blanching, changes in surface texture and gloss, partial or complete removal of paint layers, extraction of soluble components or additives such as resin or dyes, and hardening of the residual paint layer due to extraction of small molecules. Many effects can be observed directly when they are exaggerated by overcleaning or the use of inappropriate solvents. These effects also have been the subject of numerous experimental studies.

Solvent blanching can be caused by the extraction of soluble material from the paint film, the disruption of the oil-pigment bond, excessive swelling of the oil matrix, or changes in the surface texture of the paint film. Each of these actions can leave voids in or on the paint film as the solvent evaporates. These voids affect the passage of light through the paint film, reducing the degree to which pigments, dyes, and other colored materials alter the color of incident light. Thus, the observed color of the paint film is lighter and more like the incident (white) light. The effect of this blanching can be largely reversed by filling in voids on or near the surface temporarily with the application of a volatile solvent or permanently with a nonvolatile material such as varnish. The resulting darker or saturated appearance better approximates the original appearance of the paint film.

The success of treatments often is judged by the degree to which these effects can be avoided, and the degree to which the cleaned paint surface looks like a typical pristine but uncleaned paint film. The following changes in surface character indicate that the treatment has had a minimal effect on a cleaned painted surface: a smooth or glossy rather than mat surface texture after cleaning; no visible removal of paint as indicated by a lack of pigment on cleaning swabs; and a lack of blanching.

The effects of resin soaps on paint films have not been evaluated or investigated to the extent that the effects of solvents have been studied, nor are they as well-defined or understood. The reports in the literature indicate that resin soaps produce many of the same effects that solvents do. Losses in gloss are comparable to those caused by solvent exposure (7). Resin soaps extract soluble materials from paint films and in this effect are comparable to solvents (4, 7-9). Resin soaps are capable of removing paint films; therefore, special care had to be taken in swabbing especially sensitive paint films to prevent the removal of pigment during some experiments (7).

Resin soaps also differ from solvents in their effects. Resin soaps leave residues. Blanching of cleaned paint films is rarely reported. In one case blanching oc-

curred only after water was used to clear a resin soap mixture from an especially sensitive paint film rather than during the application of the soap itself (4). The lack of blanching is to some extent surprising, especially considering the possible causes of blanching noted above. Resin soaps consist primarily of water, but water and other polar or hydrogen-bonding solvents can disrupt oil-pigment bonding and produce blanching, especially in paint films with certain water-sensitive pigments (2). Resin soaps can extract material from paint films, but seem to leave no voids that would cause a lightening of the paint film. The lack of blanching, especially when factors that normally produce it are present, is initially puzzling. The probable explanation is related to the action of varnishes in darkening or saturating blanched or solvent cleaned paint films. Residue from the soap mixture could be performing the same function as a varnish, saturating and filling in the paint film matrix. Residual compounds "would help to give the paint surface an apparently 'healthy' sheen and eliminate the possibility of the slightly blanched appearance which so often follows conventional surface cleaning" (5). Indeed, color measurements of paint films before and after treatment with mixtures containing various combinations of components of resin soap mixtures show that the inclusion of *any* of the nonvolatile components produced darkening of the paint film (7). Nonvolatile materials are either absorbed into the film and reduce the effects of voids or fill in voids on the surface. In either case, the result is a film darker and more saturated than before treatment. This is an effect very different from that of solvents, indicating that the same criteria cannot be used to evaluate solvent and resin soap treatments. When a report of a treatment with a resin soap mentions that the cleaned paint film has a saturated appearance, the implication is that the treatment is being evaluated using the same criterion that is applied to paint films cleaned with solvents, i.e., that a lack of blanching implies minimal or no effect on the paint film. This criterion is not appropriate for resin soaps, for which a lack of blanching does not imply a lack of effect; it may in fact be the result of incomplete clearance of the soap mixture. More information on the relationship between the appearance of paint films, color changes in the films, and the presence and amounts of soap residues is required before more appropriate visual criteria for evaluating resin soap treatments can be established.

### Testing

Solvents have a long and continuous history of use in the cleaning of paintings. The immediate effects which they can have are known, as are the ways in which these changes might affect the painting subsequently, as in future treatments. Much effort has been, and continues to be, applied toward improving the understanding of how and why these changes take place and toward further minimizing the changes caused by solvents. The advantages of solvents outweigh the disadvantages when they are used properly.

Resin soaps as presently formulated have only a very short history of use, and an even shorter history of research into their mode of action and effects. Long-term testing becomes important because of nonvolatile residues that may have continuing effects. There are no reports yet of a painting having gone through the cycle of cleaning, varnishing, aging, and recleaning.

Much of the research that has been published brings into question some of the basic assumptions regarding how these materials work, such as their mode of action, their specificity for removal of resins, and the roles of the individual components. Dimond found that triethanolamine, rather than the resin component, was the active agent in removing an aged varnish film from a painting (10). Erhardt and Bischoff found that these mixtures affect paint films to much the same extent as solvents (although in some ways differently), and concluded that triethanolamine was responsible for much of the activity of the mixtures (7, 8). They also concluded that much of the existing literature supported a mechanism that involved solvation and extraction processes in addition to detergent action. Burnstock and Learner found that aqueous triethanolamine was relatively ineffective in removing an artificially-aged varnish film. They did find, however, that the activity of the most effective resin soap mixtures that they tested was due in large part to the presence of small amounts of benzyl alcohol.



The action of such mixtures was difficult to distinguish from the solvent effects of benzyl alcohol alone (11). Ford and Byrne found that resin soaps extracted amounts of material from paint films comparable to those extracted by solvent mixtures containing solvents such as ethanol, acetone, and toluene (9). They also found that pure triethanolamine extracted amounts comparable to those of dimethylformamide or 33% ammonia.

These results indicate the need for much more research into the action and effects of resin soaps, including the roles of the individual components. The nature and long-term effects of the residues should be evaluated. Modifying the formulae for these mixtures to minimize unwanted effects will require a clearer understanding of their cleaning mechanism and the contributions of each component.

In the meantime, some guidelines for the use and formulation of resin soaps can be proposed:

1. Solvent cleaning should be among the methods initially considered when cleaning a painting. Other methods may be considered in unusual circumstances or when no satisfactory solvent system can be found.
2. The minimum amount of nonvolatile material should be used in a formulation. Soaps should be not be used in concentrations that greatly exceed the minimum concentration required for effectiveness. Triethanolamine should not be added in excess to speed up the dissolution of resin acids when the mixtures are prepared, even if the excess is neutralized with mineral acid.
3. Unnecessary or relatively ineffective ingredients should be eliminated or minimized. If, for instance, the addition of a solvent is required for cleaning, then the possible roles of the other components should be reconsidered. Ideally, materials that have not yet been tested for effectiveness or safety should be considered for use only as a last resort.
4. Formulations should be as simple as possible, so that the contributions of individual components apparent can be more readily discerned. Modifications can then be based on a better understanding of what should be changed.
5. The amount of residue should be minimized. Appropriate clearance procedures should be followed. Formulations can be modified to minimize residues based on Wolbers' findings (6).
6. The use of mixtures containing nonvolatile materials should be avoided when cleaning surfaces that are porous or cracked. Gelled mixtures will be forced into such films by mechanical action.
7. The nature of possible residues from resin soap mixtures being considered for use should be determined by allowing small amounts of each to evaporate to constant weight under ambient conditions. Formulations that leave a residue that is mostly or totally liquid should be reconsidered.

### Conclusions

Though many similarities exist in the use and effects of solvents and resin soaps used to clean paintings, there also are many differences. In some cases, the components of resin soap mixtures contribute enough solvent activity to the soap mixture to blur these differences. Nevertheless, enough differences exist that the criteria used to judge the success of solvent treatments may be misleading when used to evaluate resin soap treatments. More work is required to determine criteria which are more appropriate for evaluating such treatments.

One of the major differences between solvents and resin soaps is the presence in soap mixtures of nonvolatile materials that leave residues. Both the short- and long-term effects of these materials require more study. Until the results of such studies are available, resin soaps should be carefully formulated in order to minimize potential problems.

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## Résumé

Les pellicules de vernis de protection représentent des liquides structurés qui, en se déshydratant, se transforment en gels solides. Ces gels ont la propriété de se gonfler et de se ramollir sous l'action des anticoagulants (l'acide oléique, par exemple). Le mécanisme du ramollissement ressemble à la thixotropie physico-mécanique et à sa "période de thixotropie"—"0".

Pour enlever les vernis de protection (huile de lin cuite à l'ancienne, vernis à l'huile) l'acide oléique liquide ou cristallin est appliqué au tampon ou pinceau sur la surface de la peinture. Après l'apparition de la "période de thixotropie" le vernis ramolli ou le repeint superposé sont éliminés au scalpel, et les restes de l'anticoagulant au white-spirit.

Les investigations ont démontré que l'acide oléique peut servir à enlever les vernis protecteurs et les repeints, il peut être utilisé en outre comme activateur ou inhibiteur, ce qui permet de diminuer considérablement la consommation de ces produits. C'est un acide bon marché.

## Mots clefs

Acide oléique, anticoagulant, thixotropie, détrempe, repeint

## Utilisation de l'acide oléique pour le décapage des oeuvres de la peinture de chevalet en détrempe du dessous des couches superposées

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Jusqu'à présent dans la pratique de la restauration des peintures de chevalet en détrempe, le choix des agents chimiques capables d'enlever les couches de vernis et les repeints tombait naturellement sur l'utilisation des dissolvants classiques protones et aprotone, polaires ou non, ainsi que sur les variations différentes de leurs mélanges. En même temps il n'existe pratiquement pas jusqu'à présent de modèle physico-chimique d'huile de lin cuite "à l'ancienne". D'ailleurs personne aujourd'hui ne peut prédire le comportement de la peinture d'auteur soumise à l'action des réactifs forts comme  $C_2H_5OH$ ,  $CH_3COCH_3$ ,  $HCON(CH_3)_2$ ,  $CH_3CON(CH_3)_2$  et particulièrement  $(CH_3)_2S$  etc. Notons également la toxicité élevée de tous les dissolvants sans exception introduits par les chimistes dans la pratique de la restauration.

Cependant une question reste ouverte: quelles propriétés doit avoir l'agent chimique utilisé pour le décapage des peintures, et plus précisément, doit-il être toujours dissolvant dans le sens propre du mot? En même temps il semble que les chimistes ne prennent pas en considération le fait que la pellicule protectrice représente une formation typiquement colloïdale apparaissant par suite d'oxydation des éthers de glycérine suivie du processus de coagulation des glycérides oxydés avec formation du liquide structuré et sa transformation par la suite en gel. Cette pellicule, à son tour, se gonfle et se triture sous l'action des anticoagulants.

Il est intéressant d'ailleurs de se rappeler le seul et unique pas en avant (sans compter licéité) fait à l'Institut I. Grabar de Moscou quand, pour ramollisseur, on a utilisé l'huile de lavande. Quoique cette expérience ne puisse pas être considérée comme toute à fait réussie, elle est sans doute utile en tant qu'essai nouveau d'utilisation pour la restauration des peintures en détrempe des matériaux apparentés à l'oeuvre. Elle a montré qu'il suffit d'observer des règles très simples pour assurer l'intégrité absolue de la peinture d'auteur et d'un autre côté, cette expérience nous a rappelé une fois de plus que l'huile de lin cuite "à l'ancienne" étant de l'huile, elle se dissout aussi dans l'huile, plus précisément, elle se gonfle, ce qui est une condition suffisante pour son élimination et enlèvement des repeints superposés.

Il semble que le résultat négatif de l'essai de l'huile de lavande s'explique par le fait que la déshydratation rapide de ce ramollisseur est le témoignage de son inutilité en qualité d'anticoagulant, ce qui à son tour est probablement dû au pourcentage élevé des glycérides d'acides avec deux et trois doubles liens, tandis que l'activité dans la destruction du gel est propre uniquement aux huiles qui ne se dessèchent pas, saturées de glycérostéarate, glycéromicérate, glycérooléate etc., ou bien à l'acide oléique libre, dont la présence dans les huiles de lin cuite, comme on le sait, détermine le phénomène du "vieillessement" et de l'apparition des craquelures sur la pellicule des huiles. Ainsi la pellicule de l'huile d'oeillette en destruction contient jusqu'à 80% d'acide oléique.

Le mécanisme d'action simplifié de l'huile de lavande se présente comme suit: en pénétrant dans la structure de gel de la pellicule d'huile de lin cuite (du vernis), la lavande donne une haute concentration de liquide intermicellaire libre et entraîne l'affaiblissement des forces van der Waalse d'adhérence des particules du gel. En définitive une désagrégation apparaît, accompagnée du ramollissement de la pellicule. Cette désagrégation est réversible, ressemble à la thixotropie avec une période égale à 0.

Ainsi, l'huile de lavande, en jouant le rôle de thixotrope physico-mécanique,

augmente l'activité du dissolvant dont elle fait partie, sans toutefois manifester sa propriété de dissolvant, car elle ne peut assurer qu'une période très courte de thixotropie vu le fait qu'elle se rapporte aux huiles se déshydratant vite.

En tenant compte de tout ce qui précède, nous avons étudié dans notre Atelier la possibilité d'utilisation de l'acide oléique dans le processus d'enlèvement des pellicules d'huile de lin cuite (du vernis) et des couches superposées.

L'acide oléique pur se présente comme un liquide incolore huileux ou des cristaux pâteux, il n'a pas de goût, possède une odeur faible et agréable, n'est pas toxique, est largement employé dans les industries des métaux, de parfumerie, d'alimentation et de médecine. C'est un acide se desséchant à demi, qui dans son état lié ou libre est présent dans toutes les huiles végétales, les huiles de lin cuite, et vernis à l'huile. Il entre comme composant principal d'huile d'oeuf dans la composition du liant des couleurs en détrempe.

Il faut souligner spécialement ici l'inertie de l'acide oléique par rapport à la détrempe, due au caractère irréversible de la coagulation des composants albumineux du jaune d'oeuf desséché. Plus loin je voudrais exposer les résultats pratiques des investigations effectuées:

La méthode d'utilisation de l'acide oléique est très simple. La thixotrope cristalline ou liquide est appliquée à l'aide d'un pinceau en poils d'écureuil doux ou d'un tampon sur la surface du fragment à décaper et, après l'achèvement de la période de thixotropie de l'anticoagulation, le vernis ramolli ou le repeint superposé sont enlevés au scalpel et les restes d'acide oléique, au tampon mouillé dans le white-spirit.

Faute de temps, je me permets de citer très brièvement quelques exemples d'essais et leurs résultats. Dans la collection du musée St. A. Roublev se trouve une icône du XVII<sup>e</sup> siècle "Aïeul Lévy" dont les vêtements avaient été repeints par une mince couche de vermillon sur l'huile de lin cuite d'auteur. Le repeint fut enlevé à l'aide d'acide oléique. De cette façon, le vermillon d'auteur, ayant une faible résistance aux dissolvants traditionnels ainsi que les ombres des contours et les contours de blanc originels n'ont pas subi de transformations visibles. Le temps d'apparition de la période de thixotropie fut égal à 10-20 minutes à condition d'irradiation du secteur traité par ramollisseur à l'aide d'une lampe de table.

Une icône du XVII<sup>e</sup> siècle "Ste Anastasie Martyre" de l'Ecole de Pskov du même musée se trouvait recouverte d'une couche dense d'huile de lin cuite très endommagée sur laquelle se trouvaient trois couches de repeints. L'oeuvre fut également décagée à l'acide oléique. De cette façon le temps d'apparition O pour l'huile de lin cuite d'auteur avec l'irradiation par la lumière de l'ampoule de microscope fut égal à 5-6 minutes et sans activation—à 20-30 minutes. L'enlèvement du repeint a demandé bien entendu une période de thixotropie plus longue, car la couche picturale empêchait la pénétration de l'acide oléique dans l'huile de lin cuite. En outre, la pellicule de protection se trouvant sous le repeint garde en règle générale une meilleure intégrité et de ce fait elle demanda plus d'efforts pour son ramollissement. Le décapage du dessous de l'huile de lin cuite très endommagée se déroula facilement sur le minium, aussi bien que sur le vert, l'ocre et la suie, qui ne manifestèrent pas de transformations visibles. La pellicule de vernis sur le rouleau résista à l'action des dissolvants tels que RT-2, alcool et autres, tandis qu'elle se ramollit facilement sous l'action de l'acide oléique. Il faut noter cependant que le contact prolongé des blancs avec l'acide entraîna leur ramollissement, qui toutefois fut facilement éliminé par le white-spirit.

Le vernis difficile à dissoudre se trouvant sur le vert et résistant à l'action des dissolvants connus a été facilement enlevé par l'acide oléique sur l'icône "La Nativité de la Vierge" (fin du XVII<sup>e</sup> siècle) de la collection du musée d'étude de la contrée de Véliky Oustioug.

Le décapage de l'icône du XVII<sup>e</sup> siècle "St Michel Archange" (musée Kigi) du dessous du repeint à la détrempe (ocre avec additions) se ramollissant avec difficulté pendant une heure et plus par dissolvant RT-2, a été fait de la manière suivante: au début sur un fragment de peinture on a appliqué une mince couche



d'acide oléique et on l'a irradié par lumière de la lampe de table pendant 20–30 minutes sans toutefois permettre le surchauffage de la surface picturale. Ensuite on a éliminé l'huile de lin cuite et le repeint superposé à l'aide d'un tampon d'ouate mouillé dans la solution d'alcool et de white-spirit dans la proportion 3:1. Après cela on a traité de nouveau les restes du repeint à l'acide oléique et on l'a enlevé immédiatement au scalpel. Finalement le fragment a été essuyé avec un tampon d'ouate à demi-sec trempé dans le white-spirit.

Enfin je voudrais citer un exemple d'utilisation de l'acide oléique pour enlever le repeint en détrempe sur or, couvert d'huile de lin cuite (l'icône "Arsène et Michel de Tver", début du XIXe siècle, musée St. A. Roublev). Le décapage se déroula très facilement, n'exigea pas de temps pour l'apparition de la thixotropie et assura une bonne intégrité de l'or. Cependant l'huile de lin cuite s'est ramolli jusqu'à une grande profondeur, c'est pourquoi l'acide oléique liquide a été remplacé par du cristallin, ce qui a permis de séparer la couche obscurcie du vernis de la couche intacte et de conserver la dernière.

Il ne reste qu'à ajouter: nous avons essayé les mélanges d'acide oléique avec les dissolvants tels que les alcools éthyliques et propyliques, le diméthylsulfoxyde, le monométhyle (éthyle) de cellosolve et RT-2. Dans tous les cas on a observé l'inhibition de ces réactifs, ce qui peut être facilement expliqué si l'on prend en considération la formation des liens hydrogènes. L'utilisation combinée de l'acide oléique et du diméthylsulfoxyde entraîne un synergisme prononcé. Ainsi l'acide oléique peut être utilisé comme inhibiteur des dissolvants aprotiques, ce qui diminue considérablement la consommation de ces derniers. L'acide est huileux et non volatil, sa consommation est approximativement égale à 0,07 ml pour 1 dm<sup>2</sup> de peinture. Il faut remarquer que si cet anticoagulant reste sur l'icône, dans 1–2 mois ou plus, la couche du vernis restant donnera des détachements, ce qui confirme la justesse de notre choix d'approche à la description du modèle physico-colloïdal du mécanisme de l'action réciproque de l'acide oléique et de la pellicule de protection. Il serait très intéressant d'examiner ce problème en détail du point de vue de la soi-disant "explosion moléculaire", mais vu la longueur limitée exigée de cette communication, cela s'avère impossible.

Pour terminer, nous voudrions attirer votre attention sur le fait que l'acide oléique permet de séparer la couche d'huile de lin cuite en destruction (vernis à l'huile) et la couche intacte. Il convient bien pour séparer la pellicule de protection et les pigments verts. C'est un réactif doux, qui garantit l'intégrité de la peinture et la santé du restaurateur.

## Abstract

In this paper Thermomechanical Analysis (TMA) measurements are reported for the first time on samples taken both from 19th century primed canvas and 19th century oil paintings on canvas. The significant parameter measured is the overall softening temperature of the composite material and the accompanying amount of compression of the sample with increasing values of relative humidity and temperature.

## Keywords

Thermomechanical analysis, moisture treatment, fabric-supported paintings, water damage

## Evaluation of Moisture Treatment of Fabric-Supported Paintings

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## Introduction

### *The effect of water on fabric-supported paintings*

The destructive action of water on fabric-supported paintings is all too familiar; basically the onset of canvas shrinkage causes dramatic flaking of paint and ground layers. This response has been observed particularly in nineteenth century paintings on commercially prepared supports. A reasonably clear understanding exists of what occurs when water comes in contact with a fabric-supported painting: water is absorbed by the canvas, causing swelling of the fibers and net shrinkage; this is accompanied by penetration of the moisture through the canvas causing an onset of softening of the size layer; the soft size then acts as a release layer, allowing the still brittle paint and ground to fracture and to be pushed out of plane by the shrinking canvas (1).

## Moisture Treatment

Water can also have beneficial effects and use is made of this property in a number of conservation treatments, traditionally as the basis of the glue/paste lining technique, and more recently with the introduction of humidity chambers and multi-purpose tables. The beneficial effects can also be used to manipulate highly fragile, brittle flakes of paint back into place. This can be a frustrating, thankless task and one which could be made simpler if the paint can be made soft and compressible. Moisture can produce this change, particularly if used together with low heat. This is not a new idea and is the basis of the treatments outlined above. They rely on an overall softening of the painting structure on exposure to humidity so that the painting can then be returned to plane. However, they lack the refinement of control and do not take into account the differential response within the painting composite. The canvas and size are highly hygroscopic and will take in water at a greater rate than the ground and paint. The latter will also eventually soften but they will reach their equilibrium moisture content at much higher relative humidity values. The potential danger of this differential response is clearly demonstrated by the evidence of water damage in paintings.

## Moisture Gradient

It has been suggested that one way of dealing with this problem is to create a moisture gradient within the painting high on the paint side and low on the canvas (1, 2). Moisture can be introduced locally from the front, using a number of methods, from simple blotting paper to water-based gels to semi-permeable membranes such as "Gore-Tex" (R) fabric. This approach has provided the basis for treating water damage locally (3). It has the advantage that it allows flexibility

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in the treatment of different areas of the painting depending on what is required. This is important for a system where there is a differential response not only within the structure of a painting but also within the different paint layers. In the case of the paint layers this depends on the pigment type, composition of the medium, and layer thickness, and implies that different areas will need different treatment times (4).

The success of the treatment lies in being able to create a permanently deformable or plastic state in the paint and ground layers, but presently only the broadest guidelines exist on how this can be achieved. If the layers in a painting are considered as amorphous or semi-amorphous polymers (5) then the change to a deformable state can be measured in the same way as it is for polymeric materials by using Thermomechanical Analysis (TMA). Previous measurements with TMA have indicated that it is possible to measure the changes which take place in unsupported paint films when they are exposed to various levels of relative humidity and temperature (6, 7). The temperatures which are measured are those of the transition which occurs from a glassy elastic state to rubbery plastic state and finally, in materials that are not cross-linked, to a state of plastic flow; or in the case of the sample from the painting, to the overall softening temperature. The measured transition temperatures will help define a framework of optimum operating conditions in terms of relative humidity and temperature.

### Background

The components of a painting (the paint layer and priming, the layer of natural glue which serves to adhere the top layer to the support, and the canvas) soften with intake of moisture, particularly if used in conjunction with low heat. Paint and ground layers need to gain their equilibrium moisture concentration at values of relative humidity much higher than that of canvas or size, potentially dan-

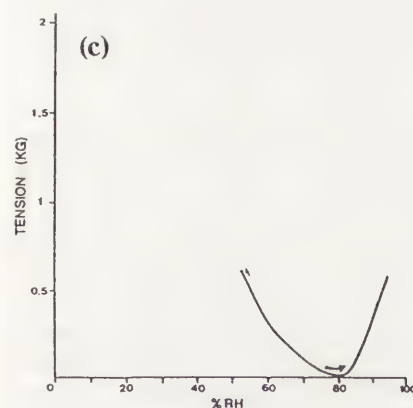
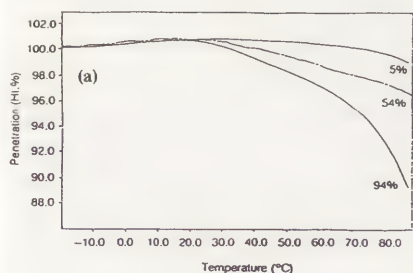
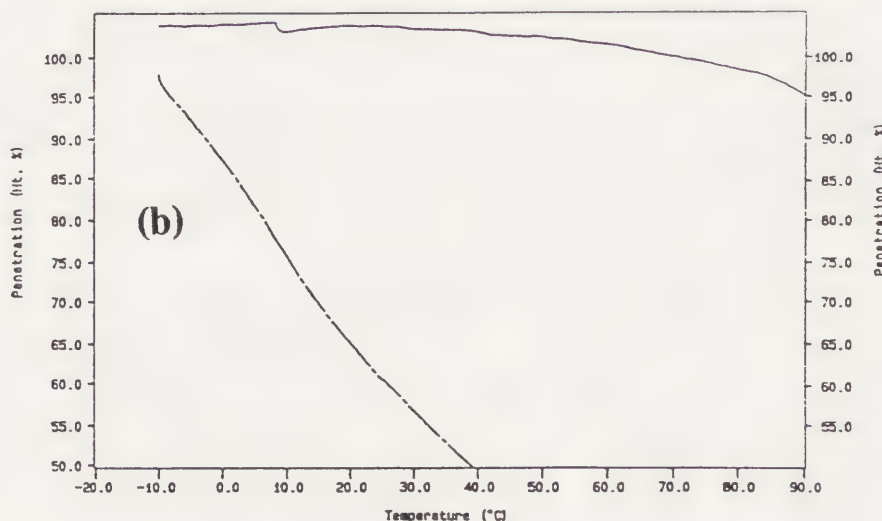


Fig 1: Response of individual layers to variation in relative humidity: (a) lead white and linseed oil: TMA compression curves for 5%, 54% and 94% RH; (b) compressibility of a film of rabbit skin glue when desiccated over  $\text{CaCl}_2$  and humidified over water; (c) onset of canvas shrinkage.

TMA Normalization: sek17  
Sample Height: 0.020 mm  
Fri Oct 27 17:25:22 1989  
RSG over  $\text{CaCl}_2/\text{Si oil}$  2a  
(Normalized)

PERKIN-ELMER  
7 Series Thermal Analysis System

TMA Normalization: sek16  
Sample Height: 0.012 mm  
Fri Oct 27 16:53:40 1989  
RSG over H<sub>2</sub>O/2 (a, b) H<sub>2</sub>O/Si oil  
(Normalized)



gerously higher, before the necessary softening of paint and ground is likely to take place. The response of the individual layers to the variables mentioned above (RH, temperature and pressure) has previously been reported (8) (See Fig. 1).

Previous work carried out by G.Hedley (9) concerned itself with the study of the mechanical behaviour during RH cycling of five naturally aged painting fragments and primed canvas samples from dates between c.1825-1912. These samples showed an overall trend exhibiting high tension in dry conditions and then progressively lower values of tension with increasing humidity, until the onset of canvas shrinkage. It was considered appropriate therefore to carry out Thermomechanical studies with varying relative humidity on the same set of samples.

## Preparation of Samples

Samples for TMA measurements were taken from 19th century primed canvases, which had previously been removed from the back of two paintings; Landseer's "Study of a Lion" and Walker's "The Old Gate" (1868/9). Further samples were taken from the removed tacking edges of paintings by Turner, "Chichester Channel" (1829), "Margate from the Sea" (1884), and "A Rough Sea" / unfinished (1835-40). The samples were 1.5mm<sup>2</sup> in size.

They were then humidified or treated with blotting paper or with a moisture gradient according to the following manner:

- (1) samples were equilibrated at 4 different values of relative humidity: 54%, 85%, 94.6%, and 97.6% RH respectively. Samples were placed in open tubes in jars containing saturated solutions of the following: Mg (NO<sub>3</sub>)<sub>2</sub>, KCl, KNO<sub>3</sub> and K<sub>2</sub>SO<sub>4</sub> for periods of at least one week.
- (2) moist blotting paper was placed on the surface for varying periods of time (30 and 90 mins).
- (3) samples were exposed to two extreme moisture gradients; low (about 5% RH) above the paint layer to high on the canvas side (over water) and then the reverse situation, high above the paint layer to low on the canvas side. These conditions were created in the following way: the sample was placed on a wire gauze over a dish containing in one case water and in the other desiccant (CaCl<sub>2</sub>).

Samples were treated with a thin film of silicone oil (Dow Corning Silicone Fluid 210/100CS) before TMA tests, in order to help retain the moisture content.

## Experimental

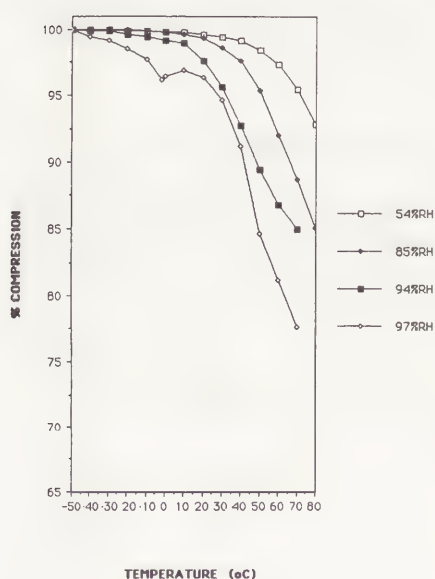
### Scanning Electron Microscopy (SEM)

The upper surfaces of one of the samples (Landseer's "Study of a Lion") were examined using a Cambridge Stereoscan 200 before and then several months after treatment. Secondary electron images were recorded using Polaroid Type 53 high contrast SEM 5" × 4" (12.5 × 10 cm) film. Samples were mounted directly on double-sided tape with at least one fractured edge unaffected by scalpel cutting. They were gold coated for three minutes using a Polaron 5200 sputter-coating unit.

Measurements were then made using Thermomechanical Analysis (TMA) in compression mode (10). In Thermomechanical Analysis a load (in these measurements 10 g or in the region of 100mN) is placed on to a sample (about 2mm<sup>2</sup> and 250μm thickness) and it is then heated at a controlled rate, in this case 5°C/min. The sample rests on a quartz platform. The results are obtained in the form of a curve (See Fig. 2).

The vertical axis gives a measure of how much the sample is compressed under this load in terms of % compression (i.e. change in thickness with respect to the original thickness). This is an indication of how much the probe moves into the sample as it softens with increase in temperature. The temperature measurement appears along the horizontal axis. The mode of operation which is used, compression mode, is one which is similar to procedures in conservation practice. The softening occurs because the composite sample passes from a hard, glassy or elastic state at temperatures below ambient through to a softer, visco-elastic or plastic state. The composite sample consists of a ground layer with or without a paint film, a layer of size and then the canvas. Previous investigations have shown that these materials have a differential response to relative humidity and temperature so that at a certain RH; the top paint and/or ground layer could be in a hard glassy state, the layer of size in a soft plastic state and the canvas may have started to shrink. The recorded TMA curves in these experiments show the overall response of the three components to temperature and relative humidity. Each sample was measured 5-6 times. The final curve which is shown represents the average of these measurements.

FIGURE 1. "STUDY OF A LION"



DETAIL/ 20-65%RH

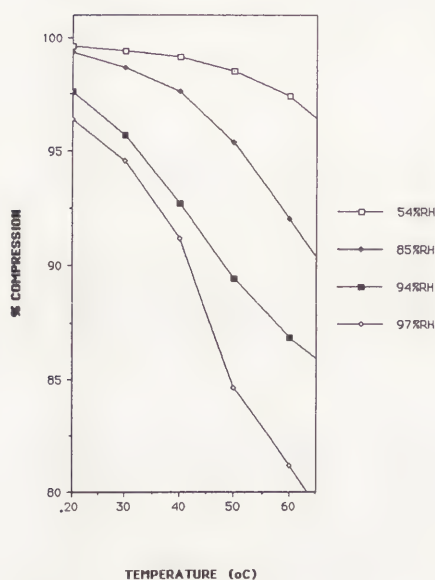


Fig 2: TMA curves of samples from "Study of a Lion".





Fig 3: Surface of sample from "Study of a Lion" spit cleaned and humidified at 54% RH.

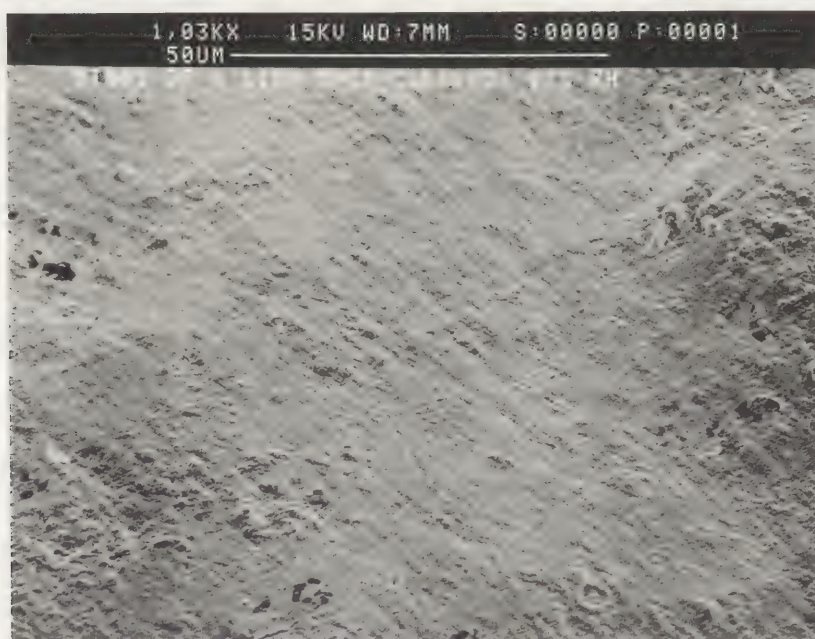


Fig 4: Surface of sample from "Study of a Lion" spit cleaned and humidified at 97% RH.

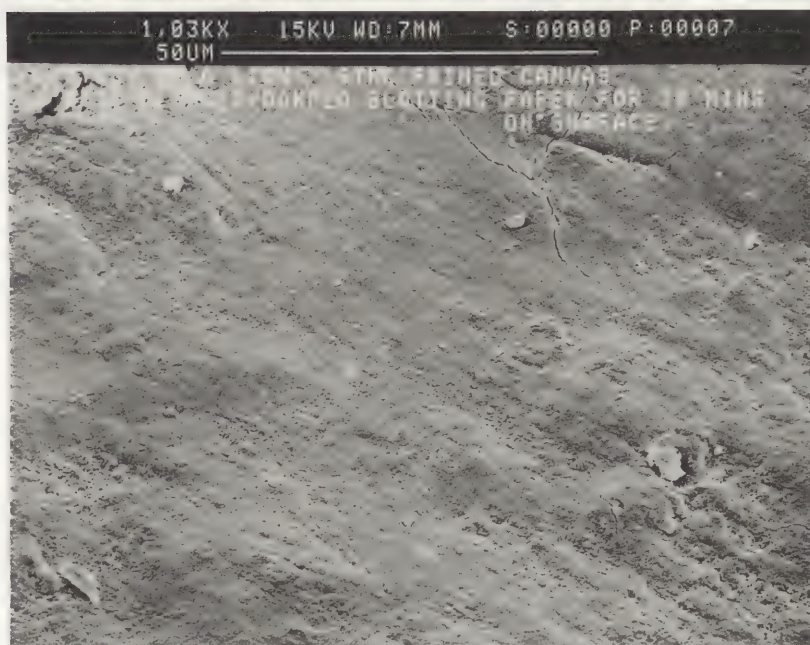


Fig 5: Surface of sample from "Study of a Lion" treated with blotting paper for 30 mins.

## Results and discussion

### Scanning Electron Microscopy (SEM)

The surface of the composite sample humidified at 54% RH and spit cleaned is shown in Fig. 3. The composite sample humidified at 97% (See fig. 4) had a smoother, more even surface than the one humidified at 54% RH. This smoother appearance could be due to the swelling and reforming of the oil medium. The sample surface also has some similarity to that of the sample treated with blotting paper for 30 minutes on the surface (See fig. 5). Differences in surface appearance correspond to differences observed in the TMA data (See Fig. 2); here the amount of softening in the sample treated with blotting paper is similar to that which was observed for samples humidified at RH values above 90%.

### Thermomechanical Analysis (TMA)

The resulting TMA curves show that the samples respond to moisture in the following manner: (1) the uncleaned sample at 54% has the highest softening temperature, in the region of 40°C, and the smallest amount of compression (2) the spit-cleaned sample treated at 54% differs considerably from that of the uncleaned and shows a behaviour similar to the one at 85% (3), samples treated at 94% and with blotter paper for 30 minutes are similar (4) samples treated at 97% and with blotter paper (90 mins) also show similarity in behaviour. These trends can be seen more clearly in Fig. 6.

The data from the TMA curves can also be re-plotted as the variation of % Compression with Relative Humidity to show the changes in the amount of softening with moisture at given temperatures. Fig. 7 shows the individual curves

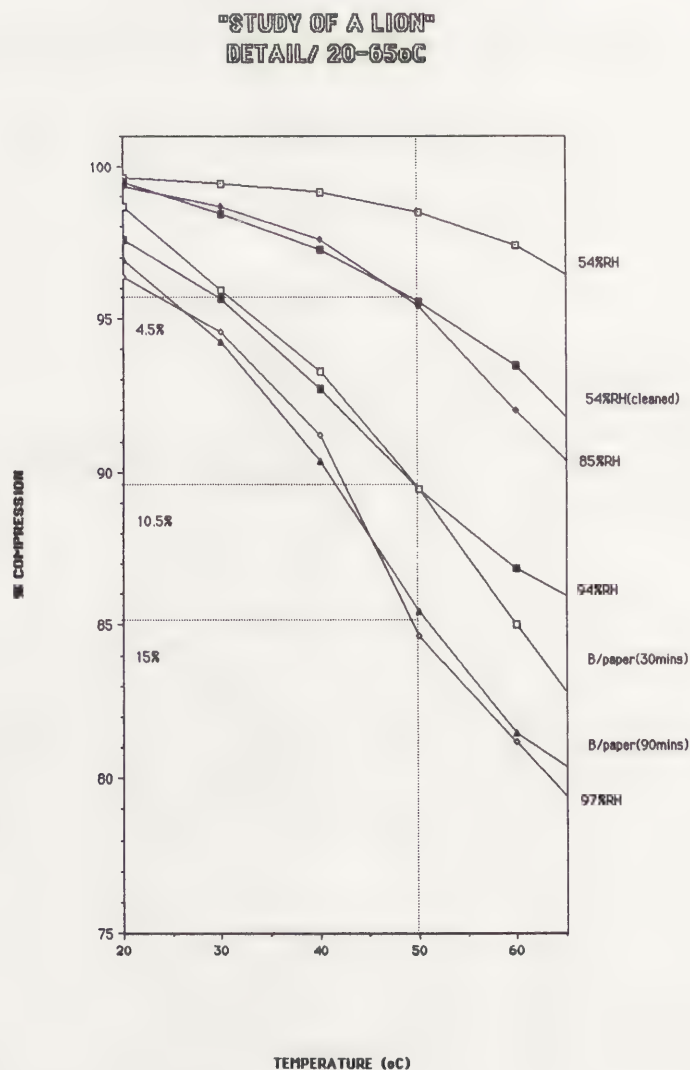
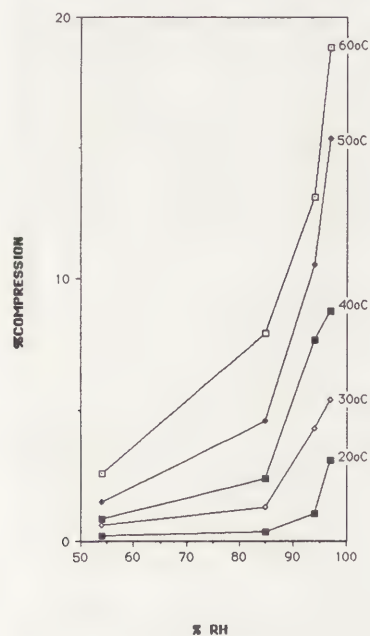


Fig 6: TMA curves of samples from "Study of a Lion".



TATE 1. "STUDY OF A LION"/ °C



TATE 1. 20/50°C

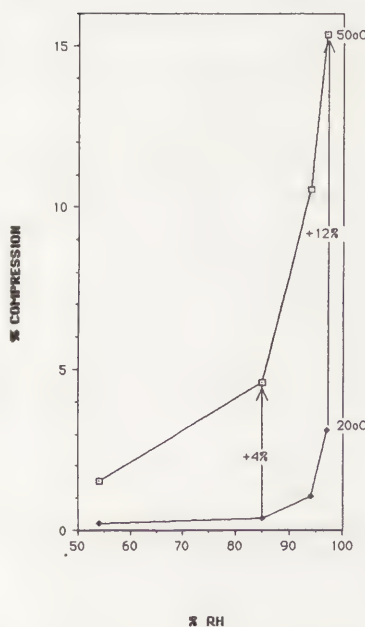


Fig 7: TMA curves of sample from "Study of a Lion" show variation in compression with RH.

plotted between temperatures 20°C and 60°C. Values for the degree of compression can be readily obtained from the curves; at 85% RH the amount of compression at 50°C is 4% higher than that at 20°C. This demonstrates that heat plays a very important role in increasing the degree of softening at any given RH; with further increase in RH to 97% this difference becomes 12%.

The overall softening temperatures are seen to decrease with increasing levels of humidification, for Landseer's "Study of a Lion" from about 40°C at 54% to 20°C at 85% and -20°C at 94%. For the purposes of this discussion the softening temperature is considered as the temperature at which the curve starts to deviate from its original position and the onset of softening of the paint composite takes place. This softening represents the contribution from all the layers. Generally in a polymeric material this transition is attributed to the onset of molecular motion in the polymer and is referred to as the glass transition temperature. In this case the sample is a composite and so the overall effect is being measured; though the glass transition temperature of one layer may have been exceeded, that of another layer may still be in the glassy state. TMA curves at 97% all showed an anomaly which was reproducible in the region of -10°C to 0°C. This may arise through the collapse of the size layer as it sinks into the canvas. In previous work (11) it has been observed that a distinct layer of size was present in the samples, indicating that they had been cold-sized.

Though results are shown only for Landseer's samples, similar trends were observed in the other cases. However, in the case of samples from "A Rough Sea" they were found on the whole to be less responsive to moisture than those from Landseer's "Study of a Lion"; this can be due to the effect of previous wax impregnation of the samples.

Preliminary work on moisture gradients demonstrated that greater softening of the composite occurred when it was humidified from below, which underlines the importance of the role of the size layer and the fact that it may assist in plasticising the adjacent ground layer.

### Conclusions

Preliminary results have demonstrated that it is possible to measure the effects of increasing relative humidity on the composite sample. It is clear that the composite is being plasticised as the level of relative humidity increases, and that at 94% RH the sample shows a significant softening which implies a loss in mechanical strength. This is consistent with the effects generally seen of water transport through organic coatings (12): a change in the mechanical and electrical properties of the coating. These are accompanied by an alteration of the coating composition (through leaching of additives, low molecular weight fractions) and a loss of adhesion from the substrate; the latter can be seen in water damaged paintings where delamination occurs and the paint layer comes away from the substrate.

Work is in progress to record the surface changes which occur, with both moisture absorption and desorption, on the upper paint layer of the composite, and the change in the composition of this paint layer. The passage of moisture through the composite is also being studied to determine precisely where the moisture goes within the structure and whether it is at any stage trapped within a layer. Preliminary results from the examination of samples in cross-section indicate that the moisture is attracted to the layer of glue which then probably softens to such an extent that it sinks into the canvas. This may explain the anomalous but reproducible effect observed in the TMA curves at high RH (97%) in the region of 0°C. The measurements obtained on the composite sample are already of some use to actual conservation treatment where it is necessary to expose selected regions of easel paintings to elevated RH values to correct deformations. TMA data gives the values for softening temperature and amount of compression which occurs. If this information is combined with what is known from previous work on the response of individual layers to increasing values of relative humidity, i.e. a sample of unsupported lead white linseed oil will soften at room canvas will shrink, then it becomes apparent that in order to plasticise the upper paint layer efficiently, it will be necessary to use a moisture

gradient where the RH values decrease from the paint layer side to the canvas. In this way the adverse effect of high RH on the canvas will be avoided. This approach has already been suggested in practice. The fact that thermoanalytical results fully support previous observations and demonstrate for the first time that the effect of moisture on such a composite can be measured indicates that localised treatment could be more precisely controlled and the mechanism of water transport through the composite understood.

The novel feature of this work is that it demonstrates for the first time that it is possible to make measurements using Thermomechanical Analysis (TMA) on samples on a canvas support and that sample size is small enough to make it possible to work with samples from actual paintings.

### Acknowledgments

The authors acknowledge the assistance of Stephen Hackney, Tate Gallery, for providing the samples, the Courtauld Institute of Art for funding Rhona MacBeth for the project, and the University of London Intercollegiate Research Service for the use of the Thermomechanical Analyser.

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### Abstract

Testing was undertaken to assess irreversible and reversible materials and systems which were thought to be suitable when used as climatic buffers for paintings on panel and canvas. Reverse coating of panel paintings, impregnation of the reverse side of canvas paintings and removable reverse side protection of canvas paintings were explored. Recommendations are made to insert conditioned ART-SORB® sheets, attach polyurethane foam sheets behind the stretcher, and provide a glass plate on the front to provide protection against extreme values of RH for several hours.

### Keywords

Canvas, wood panel, relative humidity, impregnation, painting, protection, reverse side, ART-SORB® sheets, preventive conservation

## Reverse Side Protection of Paintings—Test Results and Suggestions for a Model

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### Introduction

The protection of the reverse side of paintings against climatic effects, in particular against humidity, is one of the most important problems to be solved in the field of preservation. Restorers have tried for more than 200 years to find effective solutions to the problem. More recently, Achterkamp [1] and Beltinger [2] have provided a summary of historical developments and have given a survey of the materials and methods currently used. Their work shows the different ways used by various restoration workshops to solve the problem and to what extent other factors should be taken into account, in particular the room climate. Their investigation also shows how little theoretical work has been done in this field and, consequently, how much controversy exists among experts.

In recent years, the Department of Restoration of the Dresden Academy of Fine Arts has launched a project in cooperation with its students which is aimed at solving three main problems existing in this field. These problems are the reverse side protection of wood panel paintings, the impregnation of the reverse sides of canvas paintings and the development of a variable and removable reverse protecting element for paintings. Our aim was to test model variants which could be adapted as required to the corresponding condition.

We performed our investigation on the basis of the following reflection and experiences:

1. Wood panel paintings having the painting on one single side tend to warp and should be provided on their reverse side with a climatic buffer, the vapour diffusion resistance of which should be similar to that of the paint layer and ground. Such a buffer should be provided in order to prevent, at the same time, the reinfestation of paintings by the furniture beetle.
2. The hanging and the protection of the reverse side of a canvas painting should be performed so that the climatic values in front of and behind the painting are identical if possible (cf. Kaufmann, M. [3], Schaible, V. [4]).
3. Does the impregnation of the reverse side of canvas paintings, result in a stabilizing and hydrophobic effect, an acceptable and/or even recommendable method from the restoration point of view?
4. Is it useful to provide a removable protection on the reverse side of paintings, in particular canvas paintings, and which materials are the most suitable ones?

The authors tested reversible and irreversible materials and systems which were thought to be suitable when used as climatic buffers. The investigation considered both materials that have been used over many decades and more recent solutions.

### Reverse coating of wood panel paintings

Whereas the approximate vapour diffusion resistance of the ground and the paint layer of canvas paintings can be determined, it is almost impossible to do the same for wood panel paintings. In the latter case, the starting point of the investigation should be approximations gained from model experiments.

The following materials were tested as to their possible effect when used as a climatic barrier:

- beeswax provided with natural resins,
- shellac,
- synthetic resins (dispersed and dissolved acrylates),
- BEVA® 371.

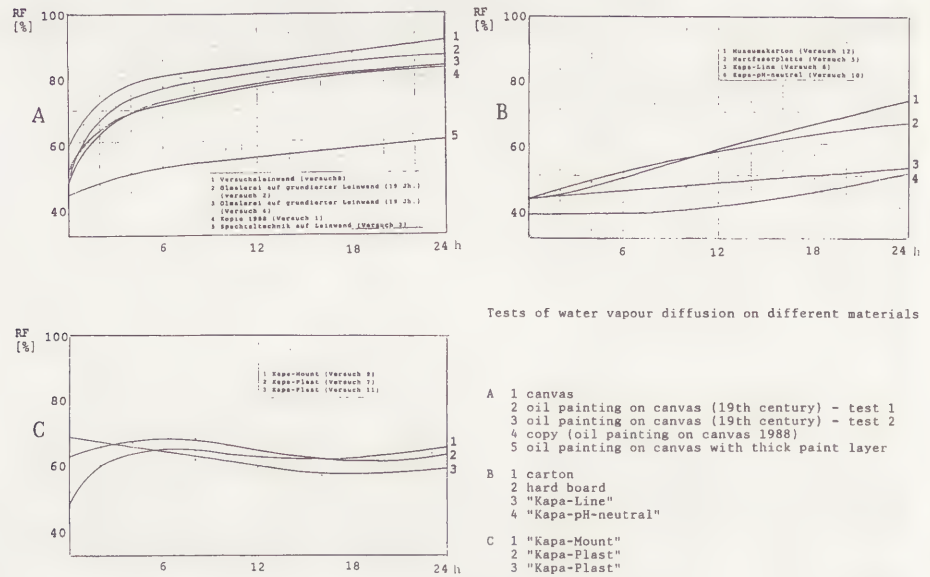


Table I. Tests of water vapour diffusion on various materials.

From the materials tested by the authors, Paraloid® B72 dissolved in toluene and Plexisol® P 550 dissolved in white spirit (with a double 10% brush application) seem to come closest to the vapour diffusion resistance of a paint layer with ground.

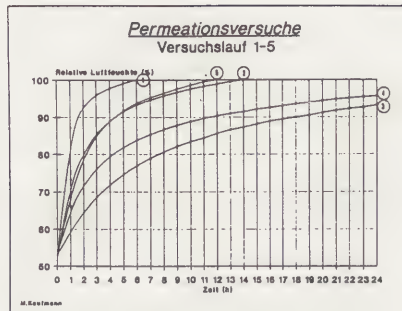
The thickness of the brush-applied coat decisively determines the resulting effect. Tests performed with films made from these materials showed that the barrier effect was better than would have been necessary. However, since there are reservations as to the use of irreversible coats on the reverse side of paintings, restorers are looking for completely reversible solutions. Because film coats are an easy technique for protecting reverse sides not only of wood panel paintings but also of canvas paintings, it is recommended that further tests be performed in future. The aim should be to find a thin and close-contact type of film having a well-defined vapour permeability.

Such films, which could be combined with a fine-meshed gauze, would at the same time prevent any new infestation by the furniture beetle, if closely stuck to the edge of the painting. The intention of the present investigation is to perform more tests in order to examine the efficiency of such a combination of climatic barrier and anti-furniture beetle protection. In the last year, a number of initial model solutions were found in connection with the restoration of large-sized wood panel paintings from the workshop of Lucas Cranach, which had previously been treated over some time with nitrogen in order to kill all active wood pests. Traditional materials, such as beeswax or shellac, which have been used for decades as brush-applied protective coats on wood panel paintings, proved to be highly efficient and obtain good results, even if applied in thin layers. However, restorers are inclined to use other materials and methods today because of the tendency of the beeswax to collect dust and/or the shellac to become brittle, with the resulting reduction of the initially good barrier effect, as well as the already mentioned limited reversibility.

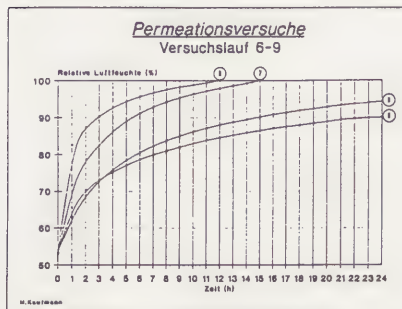
### Impregnation of the reverse side of canvas paintings

Our reflection concerning canvas paintings followed similar lines to that taken for panel paintings. We tested materials and models which are able to protect the reverse side of a painting efficiently, while being removable at any time. In addition, we performed tests on brush-applied protective coats and coatings on the reverse side of paintings.

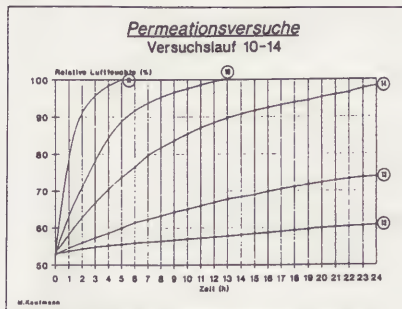
The first question that should be discussed is whether impregnations, that is the irreversible soaking of textile substrates of paintings by means of adhesive substances or buffering materials, should be used at all. We are fully aware of the devastating effects of the oiling of paintings' reverse sides and can only guess



22 Darstellung der Ergebnisse der einzelnen Permeationsversuche von Versuchslauf 1 bis 5 auf jeweils gleicher dünner Leinwand im Diagramm. 1 - lediglich mit Vorleimung; 2 - Vorleimung mit Kreidegrund; 3 - Vorleimung, Kreidegrund, darüber weißer Alkydharzstrich; 4 - wie 3, jedoch mit schwarzem Alkydharzstrich; 5 - Vorleimung, darüber weißer Alkydharzstrich.



23 Darstellung der Ergebnisse der einzelnen Permeationsversuche von Versuchslauf 6 bis 9 auf gleicher dicker Leinwand im Diagramm. 6 - mit Vorleimung; 7 - Vorleimung mit Kreidegrund; 8 - Vorleimung, Kreidegrund, weißer Alkydharzstrich; 9 - wie 8, jedoch schwarzer Alkydharzstrich.



24 Darstellung der Ergebnisse der einzelnen Permeationsversuche von Versuchslauf 10 - 14 im Diagramm. Es handelt sich jeweils mit Ausnahme von 11 um eine mit Kunstharzdispersion maschinell vorgrundete Leinwand. 10 - unbehandelte vorgrundete Leinwand; 11 - rohe, unbehandelte Leinwand wie in folgenden Versuchen verwendet; 12 - Gewebe wie Versuch Nr. 10 und 11 doubliert mit Wachsharzgemisch; 13 - Gewebe wie Versuch Nr. 10 und 11 doubliert BEVA - Film; 14 - Gewebe wie Versuch Nr. 10 und 11 doubliert mit Lascaux Acrylharzdispersion.

Table II. Water vapour permeabilities obtained by Michael Kaufmann.





Fig. 1 Basic Measuring Assembly

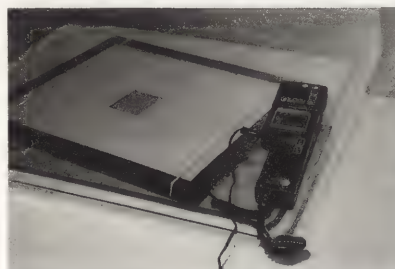
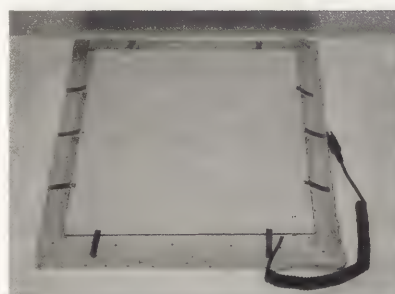


Fig. 2-4. Different Stretcher Models

the negative consequences that will confront us in future as a result of what is commonly called the "resinification" of the reverse sides of paintings. On the other hand, painting restorers know very well that the substrate of the painting is more or less inevitably penetrated by adhesive substances during the preservation of the paint layer and the ground.

Most frequently, a firm bond between the ground and the painting substrate is only possible by applying adhesive substances through the reverse side of the painting. This shows that in a few cases the precisely controlled soaking of the textile substrate of the painting, which corresponds to an impregnation, is inevitable according to the present knowledge available. As a result, it is fully justified to ask the question as to whether the proper selection of the bonding agent for preservation can provide a hydrophobic effect. The authors reject the suggestion that canvas paintings should generally be stabilized by providing brush-applied coats on the reverse side. As a matter of fact, even a low accumulation of animal glue on the textile (such as for example a 3%–4% sturgeon glue solution) can reduce the degree of climatic reaction of the textile. It is for exactly this reason that Danish restorers frequently use a weak glue solution sprayed on the reverse side of the painting. Any excess glue without the corresponding plasticizer portion will, however, result in subsequent damage similar to that caused by too much preliminary glueing.

When using synthetic resins, certain positive effects could be obtained by one or two brush applications of 8%–10% solutions of PARALOID® B72 or PLEXISOL® P 550, although protection in terms of a climatic barrier can only be obtained by applying at least two to three coats. A more efficient method would be to use brush-applied protective coats of diluted BEVA® 371 in toluene with a subsequent thermal activation. This method would also improve the preservation of the paint layer. According to the authors' experience, impregnation by BEVA® 371 can have predominantly positive effects, on ageing as well, provided that the dosing is correct. However, this type of measure should only be taken if it is absolutely necessary in order to preserve the ground and the paint layer. The mere fact that this method integrates materials irreversibly into the structure of the painting should make restorers cautious.

In all the other cases, methods such as those described above in connection with wood panel paintings should be used. In these cases, films with a vapour diffusion resistance adapted to that of the face of the painting can be placed on the reverse side without being glued. Although such solutions may be promising and although the method is completely reversible, we have concentrated our tests on the use of removable systems. The reason for this approach is that the principal problem, that is the adaptation of the climate of the near-the-wall side of the painting to the general room climate, is not solved. The maximum result that films can achieve is a buffer effect and protection against dust deposits, similar to the effect of a second canvas on the reverse side of the painting. This is a simulation of a result which can also be obtained by means of lining, for instance.

### Removable reverse side protection

The goal of our tests was to find a basic model for all types of canvas paintings that could act as a climatic buffer, bring the climatic conditions of the reverse side of the painting closer to those of the face of the painting, and act as a shock absorber, and which could be generally used and easily mounted and removed. We were fully aware that it was hardly possible to find a solution that would meet all these requirements. The following methods were used:

We tested original canvasses with various impasto-type paintings (test models and originals) as well as different sheet materials, which we thought could be used as easily removable reverse side protection, and compared the different degrees and velocities of their water vapour diffusion.

Table I shows the results achieved.

Part "A" shows the water vapour permeation through the painting over a period of 24 hours. As shown in Figure 1, the reverse side of the painting has been exposed to an atmosphere of a relative humidity of 100%. The measurement



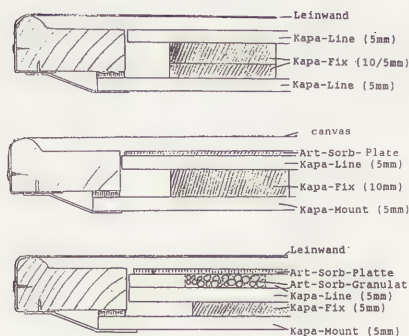


Table III. Arrangement of models.

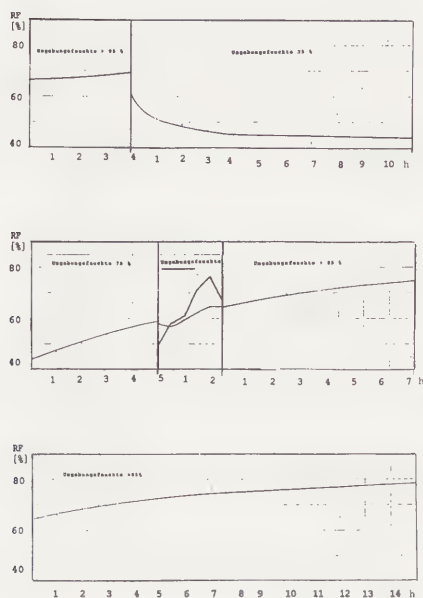


Table IV. RH variations inside the stretcher.

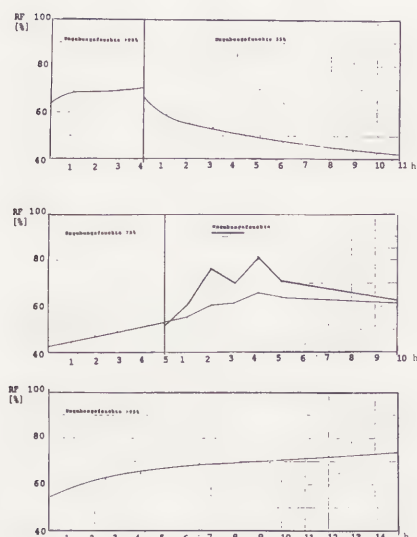


Table V. RH variations using ART-SORB®.

was performed by recording the water vapour breakthrough above the paint layer in the form of the rising RH of a closed room.

The parts "B" and "C" show the corresponding water vapour permeation values obtained on the reverse side of protection materials, such as hardboard, museum cardboard and 5 mm thick polyurethane foam sheets of the KAPA-Line, KAPA Mount, KAPA-Plast and KAPA-neutral types.

Figure 1 shows the basic measuring assembly, whereas Table I shows the results achieved.

The curves are similar to each other to a very large extent. It can be seen that the KAPA-Plast and KAPA-Mount reverse side protecting materials show a very low water vapour permeability.

On the other hand, when comparing the water vapour permeabilities obtained by Michael Kaufmann [5] on differently pretreated, grounded and coated canvasses (see Table II), it can be seen that the water vapour permeabilities of practical objects present an essentially stronger scattering than the reverse side protecting materials examined.

It was concluded that it would not be possible to choose a reverse side protecting material having approximately the same water vapour permeability as that of the painting to be protected, because the water vapour permeation behaviour cannot be evaluated without performing the appropriate measurements.

In practice, there is no doubt that the leakages of the stretcher system are the decisive factors for the exchange of humidity, as can be seen from the following tests performed by the authors.

The 5 mm thick polyurethane foam sheets can be easily handled and used as a reverse side protecting material of paintings provided with stretchers. The advantage is that this material can be mounted and removed without any problems. The material can simply be cut by means of a commercially available steel knife and fixed at the back of the stretcher easily and reversibly, by means of spring clips. We used a soft rubber profile sealing material to obtain a safe seal even on old and uneven stretchers.

In order to guarantee a shock-proof protection at the same time, models were tested where a sheet was positioned immediately behind the canvas of the painting, by means of self-adhesive KAPA-Mount strips acting as a bridge between two 5 mm thick KAPA-Line sheets. This arrangement is shown in the upper part of Table III.

Also for the purpose of testing, we cut compartments into the "shock-proof sheet". These compartments were then filled with granulated ART-SORB® silica gel and closed with ART-SORB® sheets. This method allowed us to provide additional compartments for additional humidity buffers which are intended to protect the reverse side of the painting against extreme humidity attacks in the event of climatic shocks (see Fig. 2).

In order to test the efficiency of all these variants, these stretcher models were put in compartments where the RH was controlled at a well-defined level. Sensors were provided inside the stretcher models which allowed tracking of the RH in the closed interior space of the stretcher in the event of severe climatic attacks from outside (see Fig. 3). We also considered a model where the paint layer of the canvas painting was protected by a glass pane. The removable glass pane was placed in the usual way in a wood profile frame in front of the face of the painting (see Fig. 4).

Table IV shows the variations of the RH inside a stretcher provided with a single reverse side protection (KAPA-Line sheet fixed on the reverse side by means of spring clips), the entire stretcher system being placed in an ambient humidity of 35%, 75% and > 95%.

The variations of the RH behind the canvas of the painting, measured over a period of 7 to 14 hours, are significant and give rise to the assumption that the break-in comes from the face of the painting and from the general leakage of the system.



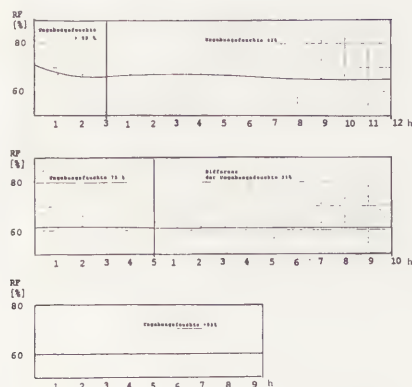


Table VI. RH variations using glass pane.

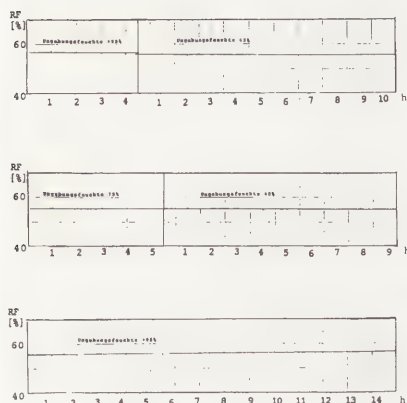


Table VII. RH variations using a glass pane and ART-SORB®.

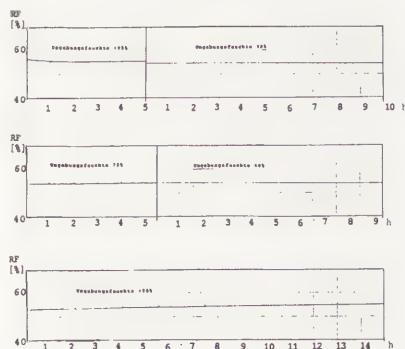


Table VIII. RH variations using a glass pane, an ART-SORB® sheet, and granulate..

There is no improvement when using additional compartments filled with ART-SORB® silica gel. The RH break-in happens spontaneously and on a wide scale, resulting in the silica gel's absorbing capacity becoming clearly insufficient (see Table V).

A considerable stabilization of the climate can be obtained inside despite any extreme outside humidity, if the painting is provided with a simple glass pane in addition to the reverse side protection of the painting (see Table VI).

An almost perfect stabilization of the RH inside the stretcher has been achieved here see Tables VII and VIII). This becomes possible if the painting is covered with a glass pane, if a simple reverse side protection is applied (as described earlier), and if an ART-SORB® sheet and/or granulated ART-SORB® is used additionally inside the stretcher.

## Conclusion

The final conclusion that can be drawn from the above is as follows. Measures that should be taken to protect the reverse side of paintings against extreme values of relative air humidity for several hours include:

- protection of the reverse side of the painting by fixing polyurethane foam sheets behind the stretchers;
- insertion of an ART-SORB® sheet of the size of the canvas, the sheet having been submitted to preliminary conditioning (or possibly used as the shock absorbing sheet);
- providing a glass pane on the face of the painting.

The reason for these measures is that, generally speaking, any dimensional changes in the different components of the painting in the event of varying RH start at the reverse side of the painting.

If no glass pane is used, all the other measures taken will become rather ineffective and the protection of the reverse side of the painting will be restricted to dust-proof and shock-proof protection. In such case, the reverse side protecting material will not be able to efficiently prevent variations of the RH inside the stretcher. The principal origins of the break-in of humidity are the faces of the paintings [cf. Kaufmann (6)] and the other leakages which can, however, be eliminated by using an ornamental frame provided with a glass pane and by taking the above-mentioned (and recommended) measures for protecting the reverse side of paintings.

## Materials

BEVA® 371: Ethylene/vinyl acetate copolymer

PARALOID® B72: Ethyl methacrylate/methyl acrylate copolymer

PLEXISOL® P 550: Butyl methacrylate (40% in petroleum ether)

Kapa-Line: Sandwich-sheet—polyurethane-foamed plastic, coated by imitation chromo-board.

Kapa-pH-neutral: Sandwich-sheet—polyurethane-foamed plastic, coated by neutral white cardboard.

Kapa-Mount: Sandwich-sheet—mutually coated by plastic-coated pulp board; amplified by aluminium.

Kapa-Plast: Sandwich-sheet—mutually coated by plastic-coated white pulp board.

Manufacturer for all products: Fa. Kapa-GmbH Lichtstoff-technik, Osnabrück/Germany

ART-SORB® silica gel: effective humidity-buffer by excellent EMC (Equilibrium Moisture Content).

ART-SORB® sheets: ART-SORB-particle coated by polyethylene/polypropylene-fleece.

Supplier: Chr. Waller—Klimatisierungsprodukte, D-W-7800 Freiburg 1, Germany

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# Working Group 3

Ethnographic Materials

Matériaux ethnographiques





### Abstract

There has been little research carried out on the materials used in the manufacture of traditionally painted Australian aboriginal objects. Their significance toward the present condition of the object as well as the treatment options have not been reported. The anthropological literature has outlined several different types of materials used in combination with pigments to decorate surfaces. These materials have been identified and a procedure developed, which has been based on Bromine-Sudan Black B staining and a biochemical identification method for triglycerides. The following procedure outlined has provided reliable results to warrant further testing on a selected group of objects from the museum's collection.

### Keywords

Binding media, paint, identification, fat, oil, lipid, staining, ethnographic

## An Identification Method for Fat and/or Oil Binding Media used on Australian Aboriginal Objects

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### Introduction

The use of materials to facilitate the painting process and bind the pigment to the substrate have been reported throughout the anthropological literature (1-3). Traditionally painted Australian aboriginal objects were manufactured using materials which fall into the 3 categories:

- 1) lipids (including animal fats such as kangaroo and goanna) and oils from plant as well as animal sources;
- 2) protein (primarily blood used ceremonially as well as egg);
- 3) carbohydrates/polysaccharides (such as gums, sugars and orchid juices).

The first group is the subject of this paper. The other two groups will be reported later.

The conservation of painted ethnographic surfaces has often been complicated by unknown materials, apart from pigment, which may be present on the surface. Experience has shown that discolouration as a result of treatment, particularly consolidation, cannot be explained by the pigment alone. Conservation considerations, such as the effect of the environment, susceptibility to pest attack, or choice of consolidant, could be better interpreted with a working knowledge of the materials in the painted surface.

It has been documented by Michalski (7) and Walston (8), that the concentrations of "binding media" used in the manufacture of ethnographic painted objects, as compared to other types of painted surfaces, is extremely low (1-5% binder volume concentration). Therefore any technique used in the determination of this additional unknown material needs to be extremely sensitive.

Through the authors' research it seems apparent that the mixing of pigment with other materials may only be to facilitate the painting process. With some pigments (e.g. iron oxides), slurries are formed with water alone, which easily separates, while others (e.g. charcoal and manganese dioxide) appear quite incompatible with water.

Australian aboriginal painted objects were traditionally made for ceremonial purposes. Often the making of the object, materials used, or accompanying ritual played the major role as compared to the finished object. Although there is no doubt as to the quality of the finished object, perhaps there was no long term intention for its durability. Therefore the term binding media may be a misinterpretation of the original intention, with the predominant role of these additions being a paint facilitator. The type used may account for some binding capability although, because it is present in such small quantities, its effectiveness as a binder can be questioned.

Therefore a project was initiated to select identification methods for these materials which could subsequently be trialled on the collection at the Australian Museum. The significance of this material with respect to the treatment of the painted surface will be evaluated after the completion of this stage of the research.

Criteria for the selection of appropriate methods were primarily based on those that could be performed in the laboratory on a routine basis and did not require advanced specialised equipment and high cost. This does not imply that there is no need to confirm some results using these services.

There is no essential difference between fats and oils except that, at normal temperatures, fats are solid and oils are liquid. They are both classified as lipids

and are chemically mixtures of triglycerides with the degree of saturation of the fatty acids relating the melting point. This also affects their stability in regard to oxidation, with unsaturated molecules being more reactive.

Several procedures were initially investigated for lipid identification, including the evaluation of Sudan Black B with or without bromination staining, Oil Red O, and the Sigma Triglyceride test (as outlined by the Getty Conservation Institute, Identification of Binding Media, developed for the course on the Consolidation of Painted Ethnographic Objects 1990). It was found that Sudan Black B with bromination and the Sigma triglyceride were the most reliable. These test methods are outlined below. For further information regarding the other tests contact the author at the given address.

### **Selected Staining Method for the Identification of Lipids**

Lipids have an affinity with Sudan dyes. It has been shown (1) that dye uptake is related to dye concentration, temperature, and physical state of the lipid, with maximal uptake occurring around its melting point (with only liquid or semi-liquid lipids being stained). Sudan dyes do have limitations; the free fatty acids and phospholipids tend to be extracted by the dye solvent while bound lipids or solid lipids remain undetected. In 1954, Lillie (2) first introduced the Bromination procedure which suppresses the solubility of the unsaturated lipids in organic solvents and converts the cholesterol to a liquid form, rendering it permeable to the dye. Therefore the Bromine-Sudan Black B procedure was found to provide a simple and sensitive method for the detection of all classes of lipids.

#### *Bromine-Sudan Black B Method for Lipids*

Method adapted from Bayliss and Adams 1972 (3)

1. Immerse paint sample in 2.5% aqueous bromine for 10 minutes at room temperature, inside a fume cupboard.
2. Wash in water and treat with 0.5% sodium metabisulphite for one minute to remove excess bromine.
3. Wash thoroughly with distilled water. (A non-brominated sample is included at this stage.)
4. Rinse with 70% ethanol.
5. Stain for 15 minutes in saturated Sudan Black B in 70% ethanol filtered just before use.
6. Differentiate with 70% ethanol until a delipidised control section appears essentially colourless. (It was found that xylene was a better solvent to clear the resin samples than 70% ethanol which softened the resin and gave it an opaque appearance).
7. Wash well.

### **Selected Biochemical Method for the Identification of Lipids**

This method involves an enzymatic hydrolysis of triglycerides to glycerol and free fatty acids. These conversions are made on glycerol to finally produce a coloured product and water. Measurement is made by the colour change produced by a quinonemine dye (5). There are some limitations in this method, as reported by Mills and White (6). Changes in buried fats can allow the converted glycerol to be washed away by water and therefore this method may not be reliable as an indicator for the presence of triglycerides. Since the reaction is reliant on the presence of glycerol and its subsequent conversion, fats will not be detected if the glycerol is leached out.

#### *Biochemical Determination for Triglycerides*

Method adapted from the Getty Conservation Identification Kit 1990 (4)

1. A sample of 0.5mg of finely ground pigment is dissolved in 0.5ml methylene chloride. This combination is mixed and then placed onto a hot plate for a few minutes until the solvent just starts boiling. Allow to cool.



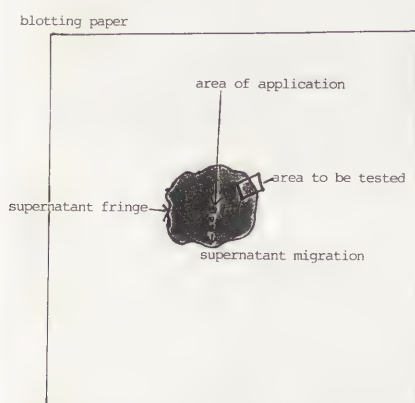


Diagram 1 Test area at the supernatant fringe

2. Centrifuge the sample for 1 minute and then remove the supernatant into a flat bottomed vial.
3. A small amount (3–5 drops) of the supernatant is then placed onto Whatman (42) blotting paper. (This step is added to give additional separation so that fine particles of pigment are separated from the supernatant which results in no false positives occurring.)
4. 0.3ml of the Sigma GPO-Trinder reagent is placed on the blotting paper at the fringe zone of the supernatant (Refer to diagram 1) and into the flat bottom vial. Allow to stand at room temperature for 10–15 minutes. A positive test is indicated by a purple to pink colour change.

### Experimental Samples

A number of different samples were made to evaluate the above tests.

#### *Test Samples 1*

Paint samples were prepared onto glass slides, using natural yellow and red ochres as well as manganese dioxide and kaolin, mixed with linseed oil to form a paint layer.

#### *Test Samples 2*

Goanna fat was prepared in a dilution series with methylene chloride at concentrations approximating 37%; 18.5%; 9%; 4.6%; 2.5% and 1.2%. Each concentration was dropped onto Whatman filter paper samples for further testing.

#### *Test Samples 3*

Cross-section paint samples were embedded into resin blocks (refer to Appendix 1). Only the staining method was used to evaluate these samples.

### Results

#### *Test Samples 1*

Samples were treated by placing each solution by a dropper onto a painted area. Both staining and biochemical tests gave clear positive results. At the same concentration, the biochemical procedure gave a stronger colour change, making it easier to interpret. The staining procedure was difficult to manipulate due to the number of steps involved.

#### *Test Samples 2*

Both the staining and the biochemical tests gave clear positive results. The sample preparation onto the filter paper was much easier to interpret than the above samples.

#### *Test Samples 3*

*Staining Only.* With the paint-embedded samples it was difficult to interpret the dark colours. This could possibly be overcome by preparing the samples into thin sections. Lipid extraction using methylene chloride onto blotting paper followed by staining could be considered.

### General Conclusions

Bromine-Sudan Black B tests were superior to the standard Sudan test when compared using the dilution series samples. Positive results were obtained with the 1.2% total fats as compared to the standard Sudan method which only detected to 18.5% total fats. Samples prepared onto filter paper gave positive results for all tests and there was better dye absorption with the brominated samples as compared to the standard Sudan samples. The extraction of lipids onto blotting paper proved to be more discernible than direct staining onto the embedded resin samples. It was difficult to distinguish a positive result, particularly for black pigment.

The Sigma biochemical procedure also provided reliable results to warrant further study. Again, extraction of the material onto blotting paper provided easily discernible results. This method can also be assessed using a spectrophotometer, as a direct measure of the concentration of the triglyceride concentration.

Unfortunately extraction, as opposed to cross sections, does not provide any information relating to layering of materials. But, in the first instance, it is more important to determine whether there is any additional material present.

### Discussion

There is no doubt that in the consolidation of paint surfaces, some changes to the surface appearance cannot be accounted for by the pigment alone. Therefore the identification of the presence of other materials may enable the conservator to better formulate a consolidation treatment, whether it be in the selection of consolidant, its application medium, or application technique.

Any further understanding of the paint surface will also enhance the selection of preventive conservation measures such as appropriate storage parameters, susceptibility to possible insect or fungal attack etc. Alteration or deterioration products may make its identification more complicated in some instances. Combinations of additional materials may further complicate identification.

Pigments were also found to be much more reactive than initially assumed. As an example, Clark and North (11) reported calcium carbonate undergoing chemical change to form gypsum, which is much more soluble in water. Limonite can also convert to hematite by heating. With the triglyceride test, it has been found that some pigments can give false positives. Therefore it was found that both tests needed to be used for positive identification. Also the introduction of the blotting paper separation for the triglyceride test helped to reduce the false positives made by the presence of some pigments. The next stage of the research is to carry out a collection survey with a series of objects selected for binding media identification. It is then anticipated that the relevance of these additional materials will further be determined. Some of these objects may be studied for consolidation treatment. It must be mentioned that consolidation must never be considered as the first option in the treatment of powdery painted surfaces, with possible support or storage options taking priority. But in some instances it is necessary.

It is the intention of a conservator interacting with museum collections to endeavour to preserve the objects and their appearance for as long as possible.

This work has been carried out as part of the Master of Applied Science in Conservation of Cultural Materials programme at the University of Canberra, Australian Capital Territory, Australia.

### Appendix 1

#### *Cross-section Sample Preparation*

A small amount of the daystar polyester resin was poured into a disposable container. The polyester hardener was added. This mixture was rocked gently in an attempt to draw the air-bubbles to the surface of the mixture and to escape before the resin is poured into the mould. Once poured into the mould the resin is again rocked gently to remove the remaining bubbles. Sometimes it will be necessary to scoop the top of the resin with a spatula to remove the bubbles. Before the resin is allowed to set, a small sample of the pigment which is to be studied is placed onto the top of the resin. The sample is then forced underneath the resin, driving it close to the bottom of the resin. Sometimes it may be necessary to pour a small amount of the resin over the top of the sample to help to force it down. Once the sample is positioned close to the bottom of the resin, the mould is then filled to the final level and allowed to set.

#### *Sanding*

This technique allows for the easier access of the pigment sample. Sanding is started with a coarse grade sand paper. The sequence is as follows: P180; P220;



CC600; rubbing on the back/smooth surface of a piece of sand paper (side without the sand), then CC1000 or CC1200. Then the sample is rubbed with an artificial chamois cloth to help to provide a smooth surface.

Inspection is carried out at various stages using the light microscope and top lighting provided by fibre optics, to gauge the pigment proximity and determine whether it is exposed on the resin surface.

### Notes

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## Abstract

Methods to cast supports for flexible sections of ceremonial costumes were considered. The sections of costume consist of flat palm spathe, decorated with pigment and seeds embedded in a resinous material. The fragile surface decoration required total support to allow inversion of the objects during casting of their undersides. This was achieved using casting plaster and liquid polyurethane foam. Since some parts of the objects are sensitive to heat, temperatures generated by plaster and polyurethane foam while curing were measured. The final support mounts were made from glass-fibre reinforced polyester resin and covered with fabric.

## Keywords

Ethnographic, storage, palm spathe, flexible, support, mould, glassfibre, polyurethane, seed



Fig. 1 Moulding underside of wooden bird effigy with P.U. foam using aluminium foil separator.

## A Support System for Flexible Palm Spathe Objects

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## Introduction

The Australian Museum has a collection of rare ceremonial costumes, collected in 1916, of the Marind Anim culture of southern Irian Jaya. They were worn for rituals connected with the sago spirit and other spirits on whom their livelihood depends. Most of the costume components are shapes cut from flat palm spathe, decorated with yellow and white pigment and with seeds embedded in a resinous compound. There are several types of seed present, but the great majority of them are from the bush *Abrus Precatorius* (commonly known as Giddy Giddy), which is found in New Guinea and northern Australia. These seeds are ovoids with a glossy bright red outer husk and a black spot at one end. In some places, the black spots have been used to create a decorative effect, by aligning the rows of seeds in alternating directions. They are extremely poisonous if ingested and the exposed kernel should not be handled without gloves.

The objects also have hanging attachments made from vegetable fibres, leaves, feathers and animal fur. In addition, there are effigies of birds, a crab and human figures, carved from wood and decorated in a similar fashion, which were worn on the body.

## Condition

During its storage since 1916, the condition of this collection has steadily deteriorated. This is clearly illustrated by comparing photographs of some pieces taken at the time of acquisition with their present state. Some components have become detached and there has been loss of the pigment. The worst problem, however, is the loss of the seeds. There is now very little adhesion between the seeds and the resin/wax and the slightest handling of some pieces results in the loss of more seeds. Whole areas of the seeds, which are in position in the old photographs, have now disappeared (See fig.1). In recent times, loose seeds have been collected and kept in bags with the objects. Unfortunately, they cannot be relocated in their original patterns, since the old photographs do not show enough detail.

The reason for the loss of adhesion between seed and resin/wax is unknown, as yet, although reference is made in the literature to the problems of ageing caused by the loss of volatile components of resins. Research is in progress to identify the resins or waxes used and the alterations which they have undergone. At least three different substances are present, with two often side by side on the same object. The seeds have been lost from areas of hard dark resins as well as from areas of softer, lighter waxy substances. Research will also be carried out to find a suitable method of holding the remaining seeds in position. At present, however, it was decided to construct storage supports to prevent the flexing of the palm spathe which causes further loss of the poorly adhered decoration.

## Methods of Manufacturing Supports

In order to create a support which can adequately follow the complicated contours of the objects, it seemed that some kind of moulding technique was the best option. Of the materials considered for the final support, the most suitable appeared to be glass fibre-reinforced polyester resin, due to its long-term stability, toughness and light weight.

The taking of moulds from museum objects for the creation of replicas or supports is well documented (1-5). However, in this instance, it was necessary



to devise a method of moulding the underside of a flexible object without disturbing the extremely delicate decoration on the upper surfaces. The two following approaches were considered.

1. The objects could be moulded from the underside without turning them over,

OR

2. The objects could be turned over and moulded normally, after first creating an accurate mould of the top side which would form an adequate support for the surface decoration. This allows inversion of the objects without further loss of the loose surface decoration and pigment.

### **Moulding Without Inverting the Object**

Experiments were carried out with two possible methods of casting the underside without inversion:

#### *Method A*

A large flat polythene bag filled with polystyrene beads was placed underneath the object and connected to a vacuum pump via a syringe needle and silicone rubber nipple on the bag. As the bag was evacuated, the beads contracted together to form an impression of the object sitting on top of them. The resulting impression was fairly rigid and the object could be removed and a cast taken of the shape. This method has the advantage of being very clean, gentle on the object and does not require the object to be wrapped in a separating layer, as it never comes close to liquid moulding compounds.

In this case, however, the method proved ineffective, as there was not enough weight in these objects to press down into the polystyrene beads to form an accurate impression as the bag is evacuated. Also, the concave underside of many of these items meant that the shrinkage of the bag resulted in its losing contact with the middle areas of the object. This method could be employed effectively on some heavier objects with a convex base.

#### *Method B*

Two-part liquid polyurethane foam (6,7) was allowed to expand upwards from beneath the object and form an impression of the underside as it set. From this foam impression, a positive cast was made from casting plaster. The final support was then cast in polyester resin from the plaster replica of the base of the object.

The object had to be very well wrapped in thin plastic food-wrap and aluminium foil and supported by several blocks of high density polyethylene foam. These blocks formed pedestals allowing the liquid to be poured under the object before it started to foam upwards. Some pressure had to be applied downwards so that the foam made contact with the entire base of the object and came up around the sides to form a complete impression.

The objects were too flexible, making it impossible to apply a totally even pressure across the entire surface simultaneously. Certain parts of the object ended up being forced upwards by the foam, creating a final impression that was not the natural horizontal shape of the object. On removal from the foam, the natural spring in palm spathe meant that it returned to its original shape and therefore could not follow the contours of the final support.

This method could be used successfully on more rigid objects which have delicate upper surfaces that prevent it from being turned over. It was used on two large bird figures from the Marind Anim collection which had carved wooden bodies and friable upper surfaces. The foam was moulded into large recesses in the underside of the bodies which were otherwise inaccessible. (See Fig.1) The resulting foam block was then moulded in hessian-reinforced plaster and a final support cast in polyester from the plaster mould. The original polyurethane foam block was not considered suitable as the storage support due to its lack of long-term stability.

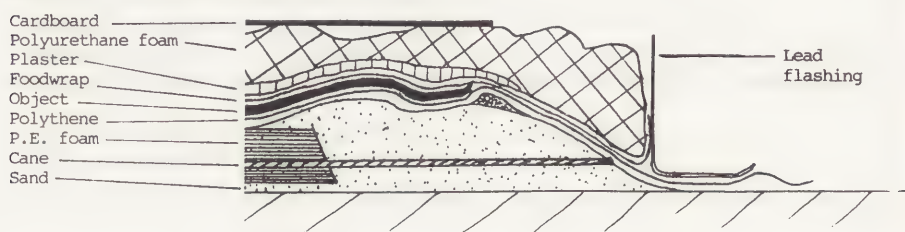
It became clear that the flexibility of the majority of the objects and their tendency to distort during moulding would also rule out other methods of casting the underside without inversion. These included floating the objects in a bath of plaster, or water-extended resin, until it hardened. The palm spathe would tend to flatten out on the surface and lose its natural shape. Trial pieces showed that this method would also be very difficult on objects with a concave base, because the casting medium will flow over the extremities of the objects, which are lower than the central area. The object will therefore become trapped as the mould hardens.

### Inverting the Object for Moulding

The failure of these experiments to produce an effective method of casting the underside necessitated a different approach. It was decided that the delicate top surface should be given total support, enabling the artifacts to be turned over for moulding. (See fig.2)

#### Cross-section of Method C Moulding System

##### STAGE 1 - Before Inversion of Artifact



##### STAGE 2 - After inversion of the artifact

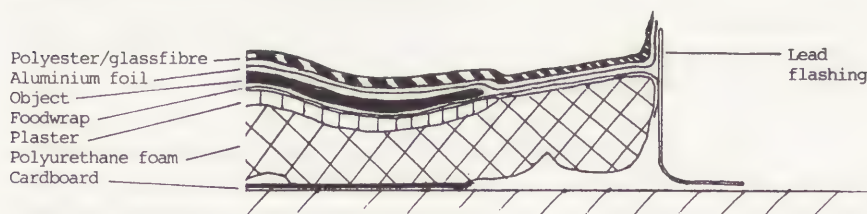


Fig. 2 Cross section of layers of method C moulding system.

### Method C

It had become evident from the previous experiments that preventing distortion of these flexible artifacts during moulding was a particular problem. Supporting the palm spathe on a bed of sand proved to be the best solution. A sheet of light-weight polythene was placed over the sand, the artifact placed on top and then the sand manipulated with hands and long brushes under the polythene until it followed the contours of the artifact. This is a time-consuming job, but essential, since any areas that are able to distort when pressure is placed on them will be moulded in this distorted position, but will spring back to their original shape when removed. This will result in the final fibreglass mount not giving total support to the object.

Once the object was supported on the sand bed, it was covered with a film of thin polyvinyl chloride food-wrap ("Gladwrap") and casting plaster poured over the surface of the object. (See fig.3) The first coat of plaster was 1-2 cm. thick. This proved to be the best method of picking up the detail of the seed-decorated surface. Other options considered did not have enough weight to flow into and around the tiny shapes. This level of detail was essential to avoid movement of the loose seeds when the artifacts were turned over.

The plaster was covered with liquid polyurethane foam, which expanded to form a light-weight block which supported the plaster and artifact. The foam



Fig. 3 Pouring plaster onto artifact protected by PVC foodwrap separator.



block could also be cut to shape very easily to form the external dimensions of the final artifact support.

With this closely moulded support for the surface decoration, the object could be carefully turned over. This was the most difficult part of the whole process, as the objects are so wide and flexible. It is difficult to apply pressure across a wide enough area to hold the whole object in contact with the support. It must be remembered that many of these artifacts have concave bases. Sliding hands beneath the polythene sheet that separates sand from artifact was difficult, without disrupting the sand and causing some parts of the object to lose contact with the upper support. To alleviate this problem, a block of polyethylene foam with a cane protruding from both sides was embedded in the sand before the object was placed on top. This allowed the ends of the cane to act as accessible grips at the edge of the mould with which to hold the polythene foam/artifact/plaster sandwich together.

### Temperature of Moulding Materials

The choice of moulding materials was limited by the costs involved. There were 25 objects and some were as large as 1.5 m.  $\times$  1.0 m. so the cost of using cold-curing rubbers such as silicone rubber was prohibitive. The heat generated during the moulding process was a real concern since the resins and waxes are very heat-sensitive. There had been indications that polyurethane foam might be too hot to be in direct contact with these artifacts. During one of the experiments to mould the underside on a bed of rising polyurethane foam, seeds and resin ended up adhered to the upper layer of polythene. It was, therefore, decided to measure the temperature of plaster-of-Paris and polyurethane foam while curing to test the theory that the plaster protected the object from the heat of the curing foam. The measurements were taken with a thermocouple attached to a digital thermometer.

**Plaster**—In two separate experiments the temperature of the plaster rose gradually to a peak 37°C and 33°C over a period of 30 minutes. The variation was probably due to differences in the temperature of the water and the thickness of plaster.

**Polyurethane Foam**—In two experiments the temperature of the foam rose to 133°C and 134°C in the space of less than 10 minutes and took an hour to drop to less than 70°C. With its good insulating properties, the foam clearly holds the heat of the reaction for a considerable time. (See fig.4)

Measurement of the temperature beneath the block of the foam gave much lower readings. For this measurement the thermocouple was placed between the foam and an "object" to give some idea of the amount of heat being transferred from the foam to the object. The results indicated that, due to the low thermal mass of the foam, the heat from the surface layers is quickly soaked up by a much denser material such as plaster which only rises in temperature by a small amount. At the same time, the core temperature of the foam remained very high, so there is a massive temperature gradient in the space of 2–3 cm. within the foam which takes more than an hour to equalise.

Having a low-density material below the foam, such as a layer of polyethylene foam, results in a much slower dissipation of heat. In two tests, this resulted in the air between the two foams expanding and pushing the polyurethane foam upwards before it had hardened, thus leaving a cavity beneath it. This could be a major problem if the foam was being used as a lightweight support for lifting a low density material.

### Casting the Fibreglass Support

When the whole assemblage was turned over, the edges of the polyurethane foam were cut to the desired outline of the final support and 2mm thick lead sheet was bent to shape around the foam to form the sides. The object was covered with aluminium baking foil and the mount was cast using 2 coats of polyester casting resin EX 301P and 230g/m<sup>2</sup> chopped strand glassfibre matt. Due to the hot summer weather (30–35°C) only 1% catalyst was used in order



Fig. 4 Measuring curing temperature of P.U. foam using thermocouples.



Fig. 5 Removal of plaster/P.U. foam top surface mould after casting of polyester backing support.



Fig. 6 Completed fabric covered support in archival quality storage box.

to give sufficient working time. Even less was used on some days when the temperatures were in the 35–40°C range (8).

When the resin was cured enough to be fairly rigid, the whole assemblage could be turned back over and the plaster/polyurethane foam block removed. (See fig.5) The aluminium foil separator, which adhered to the glassfibre, was left in place.

### Finishing the Support

The fibreglass support was trimmed at the edges with an electric jigsaw. Hand-holds were cut at the edge to facilitate lifting. The fibreglass was covered with stretch-knit cotton adhered with PVAc emulsion woodglue. The artefacts on their completed mounts were then housed in boxes constructed from acid-free cardboard with polythene foam inserts in the corner to hold the support firmly in position during carrying. (See fig.6)

### Conclusions

The work described above attempted to find the most suitable method of manufacturing closely-moulded support mounts for a group of flexible and fragile objects. The system was chosen by considering the relative importance of the following factors:

- number of objects
- size of objects
- fragility of decoration
- flexibility of substrate
- sensitivity to heat
- weight of objects
- complexity of surface contours

This method will not necessarily suit other groups of delicate organic objects. For a delicate artifact, moulding will inevitably be quite an ordeal, so the method chosen for a particular object or group of objects will be a compromise struck by assessing the relative importance of the above factors.

The Marind Anim collection is considered to be a very rare and important part of the Australian Museum's anthropology collection; therefore, it was easy to justify the investment in a good permanent support system. In the future, however, the perceived long-term benefits of permanent, close-fitting, moulded supports may result in their more general use for delicate objects. In museum collections, physical damage caused by handling, transportation and display is often the most visible type of deterioration. Physical supports and storage units that reduce the need to touch the most delicate artefacts and at the same time allow them to be accessible for study are an important element of preventive conservation.

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**Note—Health and Safety Considerations**

**Polyurethane foam** produces highly toxic isocyanate gases as it reacts. It is essential to wear a mask with an organic vapours filter when using the foam. It is also necessary to wear the mask when cutting it, as the gas trapped within the foam is released. Disposable gloves should also be worn as the foam is very hard to wash off after it has set.

**Polyester resin** also produces toxic gases and a respirator with an organic vapour filter should be worn at all times when handling it.

**Glass-fibre matting** has recently been given a higher profile as a possible health hazard. There is currently a debate as to its effects on the lungs if the fibre particles are inhaled. It is certainly advisable to wear a dust mask, gloves and cover all skin when cutting and handling glass-fibre as it is certainly a severe irritant on the skin or throat and may, as mentioned, be an even more serious health risk.

**Seeds of Abrus Precatorius** are highly toxic. Avoid skin contact with light-coloured kernel by wearing gloves when handling. If any part of the seed is ingested, medical advice should be sought immediately.

## Abstract

From ancient times to the present age, copper and copper alloys have been used extensively in making artifacts, household materials, arms and weapons. As technology is rapidly changing and only a few transmitters of this traditional technology remain, it is necessary to record the present technology of ethnological objects through field research. In this study, the elements in copper alloys were determined by chemical analysis and induced coupled plasma optical emission spectroscopy (ICP-OES). Comparative study and information about object technology may answer many questions and can aid in the preservation of historical and contemporary ethnographic collections.

## Keywords

Material culture, mould, casting, cire perdue, chemical analysis, artisan, kiln, crucible

## Technological Studies of Ethnographic Artifacts Made of Copper and Copper Alloys

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## Introduction

Applied material culture studies and the technological aspects of ethnographic metal artifacts were not sufficiently advanced in the past. Knowledge about the behaviour and modification of materials can solve many problems; it is also helpful to gain a broader understanding of the selection, adoption, and modification of raw materials to the purpose of an object. Pure copper is soft, but when alloyed it will reduce the melting point to facilitate vessel casting. In addition, the hardness of the metal is enhanced, enabling the production of artifacts, ritual vessels, and other objects. The most common copper alloys used in making ethnographic and other objects are described in Table I. The information about the second material noted in Table I (brass pital, 85Cu, 15Zn) was obtained from analytical results of contemporary copper alloys.

Table I. Typical composition of copper alloys in Bangladesh.

Material	Native name	Compositions %	Use
Copper	Tama	99Cu	Copper plate, coin, utensil, shield and ritual items
Brass	Pital	85Cu, 15Zn	All types of household and kitchen ware and crafts
Brass	Pital	77Cu, 21Zn, 2Al	As above
Brass	Varan	75Cu, 20Zn, 5Pb	Water pot, vessel, utensils, lamp stand
Bronze	Bronze	90Cu, 10Sn	Sculpture, images of god and goddess, ritual item
Bronze	Bronze	88Cu, 8Sn, 4Pb	As above
Bell metal	Kansha	80Cu, 20Sn	Plate, kanshar; a typical musical instrument, bell and other household materials

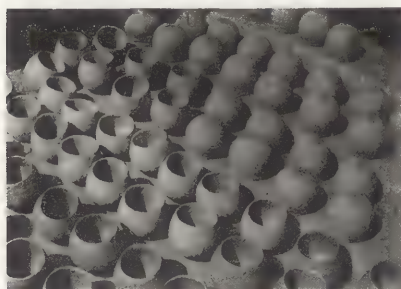
In rural Bangladesh, copper, brass, bronze, bell metals, utensils, sculptures, decorative pieces, and musical implements are very popular as a part of cultural life. Special materials were also made for festival religious ceremonies and for the purpose of worship. Among the Hindu community, kitchenware made of different copper alloys is used extensively. The Muslim in this area generally used copper wares with tin plating. The traditional old sculpture and images of gods and goddesses were made of copper alloys. There are still at least five centres in Bangladesh where these artifacts are made in the traditional way. Various types of objects are produced in Dhamrai, Savar, Kagmari, Islampur, and Chapai Nawabgonj using the indigenous technique. The skill has been handed down to them over many generations. The art of mould making, mixing metals to form alloys, and the casting and hammering processes show a strong resemblance to the ancient method known to us.

The state of metallurgical knowledge during any period is clearly reflected in the chemical, casting, and forming process used for making various images and artifacts. The chemical analysis is an important guideline, particularly to characterize the composition of the metal and to learn about the types of bronze or alloys used during the period. In addition, the proportion of different elements can shed light on the technological standard of the metal work.





1. Kiln, built with clay and plastered with mud.



2. Crucibles exposed to sun for baking.



3. Kiln fueled by wood and charcoal.



4. Preparation of moulding material.

### Information obtained from field research

Clay is one of the important materials used in the metal artefact manufacturing process. The cheapest and one of the oldest types of moulding media is undoubtedly clay. Crucibles are made from clay and kilns are built with clay and plastered with mud (see fig. 1). The earthen pot or crucible in which metal is placed for melting is locally called *Mus*. Yellow or red sticky earth is collected, mixed with rice husk, kneaded well with water, and kept for a few days in stock. The workman then made the crucible by forming the shape of a round pot and exposed the crucibles to the sun for baking (See fig. 2).

A kiln is a chamber designed to produce the high temperatures necessary for melting alloys; the structure is made with clay. The circumference is approximately 1 meter and the depth is 1.5 meters, with a hollow, round, barrel shape which has an opening at the front. In the lower part of the kiln is a netting of iron rods and an opening for the entry of air. Wood charcoal and coal are used as fuel in the kiln (See fig. 3). For mould making, white earth is collected in the dry season from the nearby lowlands and mixed with a suitable amount of sand and jute cut in a small ditch. Sand and earth are mixed in a 1:1 proportion, and 2% jute cut (by weight) is added to the mixture. Water is then poured, and the mixture is made into a paste by beating with the workman's feet (See fig. 4). It is kept wet for a few days and again kneaded, and thus making it workable. When the moulding material is ready, shaping can be achieved in three main ways: casting in one-, two- or three-piece moulds, casting by the *cire perdue* method and hammering out with repeated annealing.

The craftsman usually sits near the prepared clay and a small furnace with bellows (See fig. 5). A mixture of salt and mustard oil is used as separating agent so that the clay does not stick to the object taken for moulding. After applying the mud uniformly on the object, it is heated over the furnace to remove water from the clay. A finished three-piece clay mould of a water pot is shown in Figure 6.

The technique *cire perdue* is also called the lost wax process. It is particularly useful for easily casting metal figurines or other awkwardly shaped pieces in a mould. The object is simply moulded in wax, often around a clay core to economize on metal. The whole is then coated in clay and baked; vents are left for the molten wax to escape (See fig. 7).

There is another method of casting with a one-piece mould to manufacture a flat dish or plate for household use. Molten bell metal is poured on a mould made of clay and rice husk. This kind of mould is locally called *Aiker*, and the sheet produced in this technique is called *Dima*.

When the round sheets of bell metal are cool, four sheets are heated over the furnace fitted with bellows. Hot pieces are then placed on an anvil and hammered by at least six labourers to give the thin shape of a plate or dish. During this hammering, it is necessary to heat the metal approximately 50 times, as the bell metal disintegrates when cold.

To control the alloy proportions before putting the crucible in the kiln, the requisite amount of the metals is weighed by scale and placed in the crucible; the crucibles are then covered with clay. After the iron grill is fueled, the kiln is ignited and air is blown through the entry hole by using a fan or bellows. When the kiln becomes heated, the crucibles are placed inside the kiln with iron pliers. After that the moulds are also placed in the kiln. Gradually the temperature rises to 600–700°C, and the metals melt in the crucible.

Each mould and crucible is taken from the kiln individually to cast the liquid alloy in the mould. The casting of different sizes of objects can be done using various methods. For drinking glasses, the crucible and solid metal are put together with the mould and placed within the furnace. When the metals melt, it flows from the mould through a slit into the mould core. For spoons and bowls, the mould making and casting procedure varies.

Objects are taken out by breaking the clay mould and then taken to the workshop for smoothing the surface with files. Each object is fixed with shellac at the end

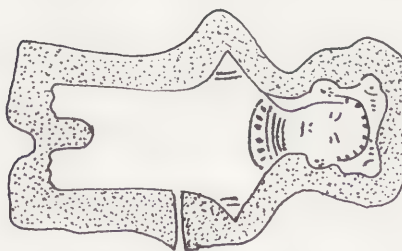




5. Application of moulding clay.



6. Finished mould of water pot.



7. Lost wax process.



8. Finishing of objects.

of a wooden roller and carefully chiseled and polished. Designs are then engraved by the artisan (See fig. 8–9).

The use of raw materials depends upon the availability of metals. At the present time, ships' propellers and rudders, and scraps of copper, bronze, and brass are used along with zinc and lead. There is a trend to add aluminium and tin to the brass alloy; for this purpose covers from empty beverage cans are being used (See fig. 10).

### Experimental results and discussion

The elements present in an artifact are generally split into three groups, major, minor and trace elements. Major elements are those which make up 2% or more of the artifacts; in most cases their proportions would have been controlled by the craftsman at the time the alloys were made. Minor elements are those present in concentrations of 0.1–2% percent, deliberately or perhaps present accidentally. Elements whose concentration is less than 0.1% are measured in parts per million (ppm); these elements may be considered trace elements. By determining the trace elements, the provenance of an object can be studied.

Approximately ten elements are identified in an ancient bronze sculpture of Bangladesh by induced coupled plasma optical emission spectroscopy (ICP-OES). ICP-OES has proved to be a very powerful method for metal analysis because of its ability of rapid and simultaneous multi-element analysis.

For analysis, each sample (10mg) was weighed and digested in 10 or 20 ml of 6N nitric acid. Any residue present was filtered off, and the solution was introduced into ICP for performing multi-elemental analysis. The results obtained in the ICP laboratory are expressed in ppm of each element within the nitric acid solution provided, and are considered to have a high confidence level.

It was not possible to directly determine the presence of tin because the residue was filtered off after digestion in nitric acid. Tin was precipitated as metastannic acid, which was then filtered off; the solution was used for ICP analysis. Chemical analysis was done and the quantity of tin was determined. The estimated amount of tin was calculated to be in the range 10–15%.

Table II. Analytical data from four ancient bronze objects by ICP-OES method.

Name:	Bowl	Sculpture	Sculpture	Sculpture
Age:	Not known	11th century	11th century	12th century
Sample no.:	1	2	3	4
	(ppm)	(ppm)	(ppm)	(ppm)
Zn	1.4	4.7	56.5	128
Pb	0.23	188	5.1	81
Co	0.24	0.37	0.04	—
Ni	0.55	0.75	0.16	0.35
Fe	3.8	3.81	3.4	0.7
Mn	—	—	0.03	—
Mg	0.06	—	0.14	0.1
Cu	100*	*p	*p	*p
Ca	1.3	1.9	1.3	1.2
Al	0.49	0.71	0.24	0.6
Ba	0.91	0.43	0.05	0.8

\* P element detected, large interference prevented quantification.

The results in Table II show that the main element present in sample 1 is copper. Copper is probably also present in samples 2, 3, and 4, but interference prevented accurate quantitation. In sample 1, the next most abundant elements present after copper are (in decreasing order) Fe, Zn and Ca, all of which are below 4 ppm. This is a completely different profile from those of samples 2, 3, and 4; samples 2 and 4 are both high in lead, but 4 is also very high in zinc. Sample 3 is high in zinc but much lower in lead. A more extensive study should be done in order to relate the composition to the origin of these artifacts.





9. Engraving of objects.



10. Beverage can covers are used for aluminium and tin.

## Conclusion

The constituents, manufacturing techniques and subsequent history of an ethnographic metal object can provide crucial information and support to the conservator. Although the word "bronze" has been used often when considering any objects made of copper alloys, without compositional analysis it can not be regarded as true bronze, brass, or bell metal. This study was based on a limited number of samples. Additional investigation and analytical data will provide more information all about these ethnographic metal objects.

## Acknowledgements

The author gratefully acknowledges Professor S.Z. Haider (Department of Chemistry, Dhaka University) for the supervision of this paper as a part of his Ph.D. research. He expresses his gratitude to Professor Stephen A. Matlin (Department of Chemistry, University of Warwick, England) and his colleagues for providing the ICP-OES analytical data. In the Bangladesh National Museum the author is thankful to Mr. Anowarul Haque (Keeper), Mr. Khatibul Huda (Conservation Chemist), and Mr. Tarun Ghosh (Assistant Keeper) for their comments and discussion.

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## Abstract

Tanning procedures cause changes in the appearance of skin. These changes can be associated with changes in the inherent properties of skin, such as fatty acid composition and shrinkage temperature. This paper describes fatty acid composition and shrinkage temperature at different stages through an Inuit tanning procedure, comprising stretching, scraping, and chewing of skins originating from ringed seal (*Phoca hispida*) and caribou (*Rangifer tarandus*). Significant decreases in the content of unsaturated fatty acids were noted with a simultaneous increase in the shrinkage temperature, thus demonstrating the effectiveness of the tanning procedure. The implication of these findings on the state of preservation of actual items of Inuit skin clothing is discussed.

## Keywords

Inuit, tanning, skin, fatty acids, shrinkage temperature

## On the Changes of Skin Characteristics Through an Inuit Tanning Procedure

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## Introduction

One of the world's largest collections of archeological and ethnographic items of Inuit origin is found at the National Museum of Denmark in Copenhagen. The most important and most well-documented collection of items was obtained during the Fifth Thule Expedition (1921–1924) on its journey through arctic Canada (1). A significant part of the collection consists of skin clothing. Typically, Inuit skin clothing was prepared using skins of seal or caribou.

Scrutinizing the individual items revealed significant differences in appearance, e.g., colour and stiffness, which supposedly could be related to the state of preservation (2).

Obviously, the tanning procedure will introduce a variety of changes in inherent skin characteristics. Prior to a detailed analysis of items from the above-mentioned Inuit skin clothing collection, it appears crucial to elucidate the effect of the Inuit tanning procedure on skin characteristics. This procedure traditionally involves stretching, scraping, and chewing. Thus, this paper describes the variation of inherent skin characteristics, exemplified by fatty acid distributions and shrinkage temperatures as a function of tanning.

In the present study two types of skin, originating from ringed seal (*Phoca hispida*) and caribou (*Rangifer tarandus*), were studied.

## The tanning procedure

The Inuit bands in the central arctic areas of Canada applied different tanning procedures for seal and caribou skins. However, a common feature for all the procedures was that no tanning agent was applied to the fresh skin. Thus, Hatt reported that the fat present in the skin is oxidized to fatty acids, which interact with the fibers in the corium as is the case through the fat-tanning procedure (3). It was, however, emphasized by Parry that the eventual result was strongly dependent on the skill of the individual tanner (4). In the present study, analyses were carried out on fresh skin samples, at different stages of the tanning procedure. In the case of seal skin, analyses were carried out on the following preparations: 1) dried and stretched skin, 2) dried, stretched, and scraped skin, and 3) dried, stretched, scraped, and chewed skin. The analyses of caribou skin were carried out on the following preparations: 1) drying and stretching, and 2) drying, stretching, and scraping. In the case of caribou skin, both hairy skin and skin de-haired by fermentation were studied.

All samples were prepared during a course on Inuit skin preparation organized by the Canadian Conservation Institute, held in Churchill in August, 1989 (5).

## Fatty acid analyses

In nature, fat is present in a variety of forms. In animal cells and tissues, fat is often found in combination with other organic components, e.g., as triglycerides.

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The fatty acid distribution appears as a combination of saturated, monounsaturated, and polyunsaturated moieties, the mutual ratio being typical for the single species. The mutual ratio between the single fatty acid moieties can be affected by the tanning procedure. However, exposure to daylight may influence the fatty acid distribution. In both cases, the so-called auto-oxidation appears responsible for the disappearance of the mono- and polyunsaturated fatty acid moieties. It is in this context emphasized that the auto-oxidation leads to lower acids as well as aldehydes. Thus, the process does not lead to a simple saturation (6).

For fatty acid analysis, a 2 mg sample of tissue (corium) was cut into fine pieces and mixed with 0.5 ml tetrahydrofuran (freshly distilled, not stabilized). After 12-18 hours, the suspension was sonicated for 0.5 hours in an ultrasonic bath to achieve complete homogenisation.

Transesterification of the triglycerides was accomplished by adding 1 ml of a NaOCH<sub>3</sub> solution (ca 3 g of metallic Na in 100 ml methanol) to the sample. The sample was left for 0.5 hours in an ultrasonic bath. Subsequently, 1 ml of a NaCl solution and 1 ml of a concentrated H<sub>2</sub>SO<sub>4</sub> solution were added to the preparation.

The fatty acid methylesters was extracted with pentane. The pentane phase was dried with Na<sub>2</sub>SO<sub>4</sub> and evaporated to a volume of ca 100µl. The concentrates were analysed on a Hewlett-Packard HP 5890A gas chromatograph equipped with a FID detector. The analyses were carried out using a CP-Sil 88 column (Chrompack), using helium as the carrier gas. The identification of fatty acid methylesters were established by comparison with standard solutions analyzed under similar conditions.

Significant differences in the fatty acid distributions in skins from seal and caribou were noted. In Table 1, the distributions of the acids are given as the relative amount of saturated, mono-, and polyunsaturated fatty acid moieties in skins originating from seal and caribou. The obtained values are in good agreement with previously reported values for seal blubber and caribou fatty tissue (7-9).

The predominance of mono- and polyunsaturated fatty acids in seal skin is immediately noted in contrast to the relatively high content of saturated species in caribou skin. In Figure 1, the fatty acid distribution at the different stages of the tanning process of seal skin is illustrated.

Table 1. Fatty acid distribution (in pct.) in skins originating from seal and caribou.

	Seal	Caribou
Saturated	9.6	38.7
Monounsaturated	65.0	52.7
Polyunsaturated	25.4	8.6
Unsaturated (total)	90.4	62.3

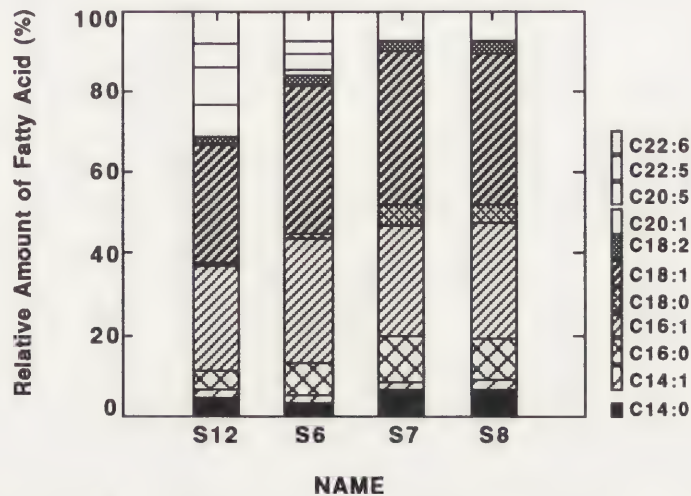


Figure 1. Fatty acid distribution in seal skin at different stages of the tanning process. S12: untreated hairy skin; S6: hairy skin, dried, and stretched; S7: hairy skin, dried, stretched, and scraped; S8: hairy skin, dried, stretched, scraped, and chewed.

In the sample of untreated skin (S12), the distribution discloses the high concentrations of mono- and polyunsaturated fatty acids. It is immediately noted that the drying and stretching process causes a distinct decrease in the relative

amounts of the unsaturated part of the fatty acids, although all species still can be recognized. On the other hand, scraping, the second stage of the tanning procedure, virtually removes all polyunsaturated acids except C18:2. Surprisingly, chewing, the final step in the seal skin tanning process, apparently did not change the fatty acid distribution, although significant changes in the subjective appearance of the skin were noted, such as increased softness. It is noted that the relative amounts of monounsaturated fatty acids appear more or less constant during the tanning process. The apparent disappearance of the unsaturated fatty acids during the tanning process may partly be due to a physical process, in which the scraping removes the less viscous part of the triglycerides.

A somewhat different picture develops in the case of caribou skin. Figure 2 depicts the fatty acid distributions in caribou skin at the different stages of the tanning process. The figure summarizes two different tanning procedures: 1) tanning of the hairy skin by stretching and scraping, and 2) tanning of a skin de-haired by fermentation.

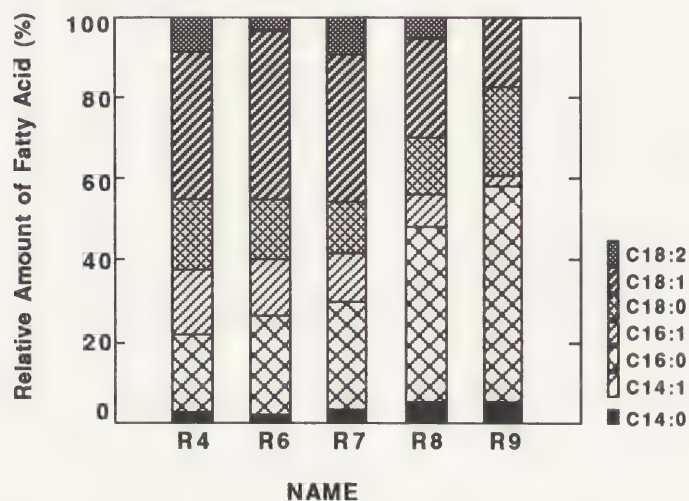


Figure 2. Fatty acid distribution in caribou skin at different stages of the tanning process. R4: untreated hairy skin; R6: hairy skin, dried and stretched; R7: hairy skin, dried, stretched, and scraped; R8: de-haired skin, dried, and stretched; R9: de-haired skin, dried, stretched, and scraped.

It is noted that the tanning of the hairy skin (compare R4, R6, and R7) apparently leads to only minor changes in the fatty acid distribution. Thus, the relative amounts of C16:0 and C16:1 were slightly shifted in favour of C16:0, whereas the corresponding C18:0/C18:1 ratio remained virtually constant. In contrast, the tanning of the de-haired skin introduced significant changes in the fatty acid distribution, as pronounced relative increased concentrations of the saturated fractions are noted (compare R4, R8, and R9). Apparently, the de-hairing process (fermentation) caused a major oxidation of the unsaturated acids, resulting in the apparent relative increase in the content of saturated acids.

### Shrinkage temperature analyses

The shrinkage temperature is defined as the temperature (in water) at which the collagen in skin denatures and is irreversibly destroyed. During the denaturation the material shrinks to approximately 35% of its original size. The shrinkage temperatures of fresh skins of mammals range from 62° to 68°C, whereas tanned material exhibits shrinkage temperatures at or above 100°C (10).

A small portion of fine, dispersed material was degreased with a few drops of acetone. The degreasing appears essential in order to ensure the subsequent saturation of the fibers with water. Before the acetone was evaporated, 1 ml of distilled water was added and the sample was left for 15 minutes in order to achieve complete swelling of the fibers, as swelling influences the stability of the collagen until equilibrium is achieved. Thus, the shrinkage temperature is a measure of the remaining stability of the collagen (10).



The shape of the fibers as a function of increased temperature was examined under a microscope during shrinkage. The samples were placed in sealed, hollow-grounded object glasses to secure free movement of the fibers without evaporation of the water. The samples were heated on a Mettler FP 82 HT Hot Stage with a gradient of 3°C per minute and controlled by a Mettler FP 80 HT Central Processor. Before denaturation, the fibers were silver-shining, transparent, and crystalline, with slightly folded bands. The progressive denaturation under increasing temperatures was recognizable through the decreasing transparency and increasing shrinkage of the single fibers. We have defined the initial shrinkage temperature ( $T_i$ ) as corresponding to the point at which approximately 50% of the fibers having lost their transparency. The final temperature ( $T_f$ ) is defined as the point at which approximately 90% of the fibers are denaturated. The quantity  $T_f - T_i$  is defined as  $T_d$ . An effective tanning will be recognized as an increased  $T_i$  and a small  $T_d$ .

In Figures 3 and 4, the shrinkage temperatures for the skin samples correspond to the single stages of the tanning processes.

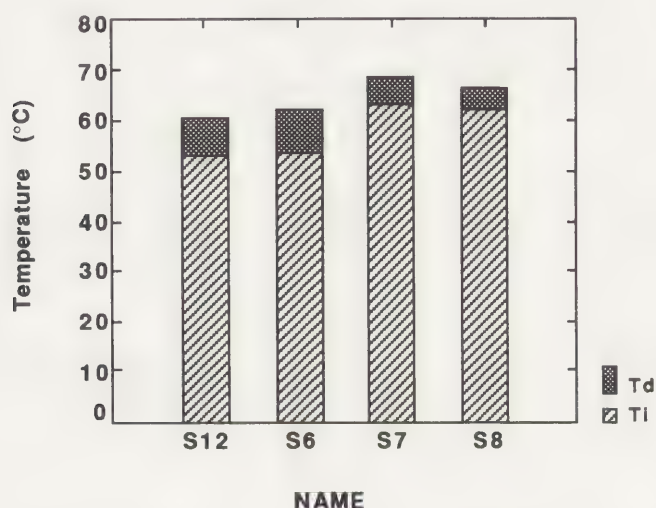


Figure 3. Shrinking temperature ( $T_i$  and  $T_d$ ) for seal skin at different stages of the tanning process. S12: untreated hairy skin; S6: hairy skin, dried, and stretched; S7: hairy skin, dried, stretched, and scraped; S8: hairy skin, dried, stretched, scraped, and chewed.

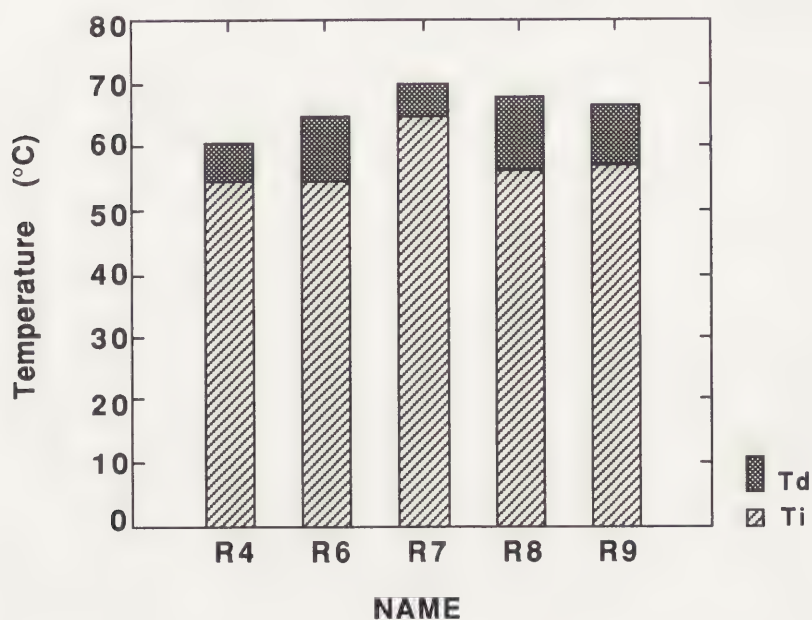


Figure 4. Shrinking temperature ( $T_i$  and  $T_d$ ) for caribou skin at different stages of the tanning process. R4: untreated hairy skin; R6: hairy skin, dried, and stretched; R7: hairy skin, dried, stretched, and scraped; R8: de-haired skin, dried, and stretched; R9: de-haired skin, dried, stretched, and scraped.

In the case of seal skin (Fig. 3) it is seen that the shrinkage temperatures of the untreated skin (S12) and the dried and stretched skin (S6) are virtually identical, whereas the shrinkage temperatures of the skin samples corresponding to the second and third stage of the tanning process are significantly increased by approximately 10°C ( $T_i$ ) and 7°C ( $T_d$ ), respectively (See fig. 3). Thus, the effectiveness of the tanning process is reflected both in an increased  $T_i$  value and a decreased  $T_d$  value. It is noted that the final chewing process only has a minor influence on the shrinking temperature and, hence, the tanning effectiveness. This is in agreement with the above results on the fatty acid distribution at the different stages of the tanning process (cf. Fig. 1).

A similar trend is seen in the case of the tanning of the hairy caribou skin (Fig. 4, compare R4, R6, and R7). Following the scraping an increase of approximately 10°C in the  $T_i$  and  $T_d$  values are noted (R7). In contrast, the  $T_i$  values for the two stages of the tanning process of the de-haired skin are identical to that of the untreated skin, whereas the  $T_d$  values are increased by approximately 5°C, indicating degradation of the skin fibers (Fig. 4, compare R4, R8, and R9). Most probably this feature can be associated with a negative effect of the de-hairing process, which to a certain extent apparently is compensated by the scraping.

### Conclusion

Inuit tanning procedure significantly influences the fatty acid distribution in seal skin. The fraction of saturated fatty acids is strongly increased at the expense of the unsaturated species, probably due to auto-oxidation of the latter. In particular, the polyunsaturated fatty acids are removed through the tanning process. In the case of caribou skin, the variation in the fatty acid distribution is less significant, although a pronounced effect of the de-hairing process occurs.

The effectiveness of the tanning process is likewise demonstrated by the increased shrinkage temperatures observed as the tanning process progresses. However, the negative effect on the caribou skin of the de-hairing process is also reflected in the determined shrinkage temperatures; the increased  $T_d$  values suggest degradation of the skin fibers.

Obviously, the variations in fatty acid distributions and shrinkage temperatures as a result of the tanning process have to be taken into account if these factors are to be used as a measure for the state of preservation of actual Inuit skin clothing.

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# Working Group 4

Documentation

Documentation





## Abstract

Describes a literature survey, occasioned by a research project into the problems of consolidating matte, friable paint, with an emphasis on ethnographic objects. Available bibliographies and databases, such as BCIN, CAS, and RAPRA, provided few references.

Although few references were initially located, isolating the problem's physical nature and understanding its interdisciplinary aspects aided in identifying and compiling a wide variety of literature of direct relevance to the problem and useful to the conservator in designing treatment strategies. Annotated references to this literature have been gathered into a topical supplement to *Art and Archaeology Technical Abstracts* (AATA), to be published autumn 1993. The organization, sources, and unique aspects of this bibliography are described in this paper, as is the research methodology used to assemble the references.

## Keywords

Bibliographies, interdisciplinary research, consolidation, paint, matte, ethnographic objects, databases, flaking

## An Interdisciplinary Bibliographic Approach to a Complex Conservation Problem: The Consolidation of Matte Paint

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## Introduction

In 1988, the consolidation of painted ethnographic objects was identified by the GCI as one of the currently most difficult treatment problems the conservator encounters, especially when matte, friable surfaces must be consolidated. The literature on this subject was surveyed as a first step in conducting scientific research to analyze the problem and evaluate existing treatment methods.

Scientific studies at the GCI, both experimental and analytical, indicated that many investigators based their work on incorrect assumptions of the physical nature of the problem. Factors that affected the *treatment methods*, and the distribution of the consolidant within the paint during application, were found to be more important than a comparison of properties of individual consolidants. The particular problem of discoloration was addressed by considering the physical and optical properties of high pigment volume concentration paint (paint which has a low ratio of binder to pigment), and how such a system behaves when a consolidant is introduced.

In considering the interdisciplinary nature of the conservation of painted objects, particularly the consolidation of porous, matte paint, the authors proposed a special supplement to AATA because, in their experience in identifying literature relevant to this problem, a dearth of references were readily available as a basis for research. This bibliography, *Matte Paint: Its History and Technology, Analysis, Properties, Deterioration and Treatment (with Special Emphasis on Ethnographic Objects)*, (to be published autumn 1993) adds literature from the fields of anthropology, ethnobotany, art history (artists' notes, interviews or descriptions of working techniques) and coatings science to AATA, which had scant previous coverage of these fields, in addition to collecting in a single volume relevant literature from the fields of chemistry, archaeology, and conservation.

Solutions are presented to the problems involved in the acquisition and evaluation of literature from a large number of fields which, at first glance, might appear unrelated to this conservation concern. A primary problem is that the interdisciplinary nature of conservation makes it difficult to identify a standard body of literature for research.

Preventive conservation, usually the first line of defense, and ethical considerations were not included in the scope of this bibliography to maintain the focus and restrict the number of references possible in a single volume.

## Background

The focus of the supplement is on the problems and conservation requirements of painted surfaces when the paints contain little or no binding media. These paints, often referred to as having a high pigment volume concentration (PVC), are characterized by their poor cohesive and adhesive properties. They normally have a matte appearance and are often in a powdery, friable or flaking condition. Their treatment requirements differ from paints containing high proportions of binding media (such as used in oil paintings) in that consolidants are easily absorbed into the paint and fill voids between pigment particles, with consequent changes to appearance and practical irreversibility of the treatment.

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The aim therefore, when consolidating porous matte paint, is to use a consolidation system that distributes the consolidant in a manner that minimizes changes in appearance, introduces the minimum quantity necessary to achieve effective cohesion of the pigment particles, and is compatible with the paint and support materials in the long term.

In an initial attempt at literature identification, over 100 practicing conservators in the United States (listed in specialty index of the 1988 *Directory of the American Institute for Conservation of Historic and Artistic Works* under ethnographic objects) and abroad were individually interviewed. Coatings and conservation scientists were also interviewed and BCIN was searched with keywords relating to the conservation of ethnographic painted objects. Very few directly useful references were found in the ethnographic conservation literature, forcing a search for applicable material in other fields of conservation (paintings, polychrome sculpture) and in the coatings and chemical fields.

In assessing the reasons for deterioration, it became necessary to search the anthropological literature for descriptions of techniques or materials used in manufacturing paint of a high PVC. In addition to elucidating possible reasons for deterioration, this knowledge is also of use in planning treatments and selecting consolidants. A general article on literature sources useful for bibliographic research for conservators was produced during the process of this project (Bishop 1992).

### **Literature Support Needs and Sources**

The literature support needs were:

- 1 To isolate problem geographic or cultural areas where matte paint was prevalent;
- 2 To identify materials and methods of making objects in order to reproduce them in the laboratory;
- 3 To understand the physical nature of the problem (explain why matte paint discolors when consolidated);
- 4 To understand the methods of deterioration of matte painted objects; and,
- 5 To understand the parameters affecting the treatment and develop methods to evaluate treatment methods and materials (develop quantitative comparative evaluation techniques).

To meet these needs an extensive campaign of bibliographic surveys was begun. After identifying the various disciplines to investigate, a search for bibliographic tools in these areas was initiated. The initial focus was computer databases, abstracting and indexing services, and bibliographies. Our initial strategy was to compile a large body of relevant citations that would then be examined further. Early on, it was decided that every item cited in the bibliography would be reviewed, which meant a hard copy of the article had to be acquired. Fortunately, we had access to two excellent libraries, the library holdings of the J. Paul Getty Trust and the University of California at Los Angeles (UCLA). Whenever we were unable to obtain needed material from either of these libraries, most literature could be obtained through the inter-library loan services of the Getty Conservation Institute Library. With these resources at our disposal, a very high percentage of the material that was sought was obtained. Then abstracts were written when they were lacking or existing abstracts were reviewed and revised to address our specific interest in matte painted surfaces. The authors found themselves in the rather unique position of poring over important anthropological literature searching for mentions of how paints were made. During the bibliographic research period we found excellent material but were frustrated in our use of computer databases by the absence of standard terminology.

### **Literature Searches using Keywords**

A core bibliography of approximately 100 references existed as a result of developing the course. An initial search was conducted using the bibliographic database of the Conservation Information Network (BCIN), Chemical Abstracts (CAS) and World Coatings Abstracts with a variety of keywords: paint dete-



rioration, matte paint, paint consolidation, etc. However, a pivotal reference is "The Lightening and Darkening of Porous Paint" (Feller and Kunz 1984). This could not be located with these keywords; one had to use 'porous'. These searches were most successful for the analytical and properties section, and for assuring that the treatment section would be comprehensive. The lack of standard nomenclature in conservation dictates a very flexible searching strategy.

### Traditional Bibliographic Sources

Another source was individual, traditional format bibliographies. For example, BCIN covers AATA but does not completely cover important early publications such as *Technical Studies in the Field of Fine Arts* (William Hayes Fogg Art Museum 1932–1942) or the abstracts that appeared in the back of each issue of the journal. *Abstracts of Technical Studies in the Field of Fine Arts*, published by the Freer Gallery of Art in 1955 has not been systematically incorporated in BCIN either. It should also be noted that the special supplements to AATA have not been incorporated into BCIN. Since the resumption of supplements to AATA in 1991 citations in supplements are routinely incorporated into BCIN.

AATA remains the only abstracting and indexing service in the conservation field. Although its scope is interdisciplinary it is impossible for a publication that relies on volunteer abstractors to cover the relevant literature comprehensively. Relevance is not always readily apparent and the degree of relevance varies. Literature in the history of technology is a good example. An understanding of the technology available to groups of people who made artifacts can be very helpful in general but may not be relevant to a specific technical problem.

A number of other important sources were used as a source of citations. *Bibliographia Antiqua; Philosophia Naturalis* (Nederlandisch Institut voor het Nabje Oosten 1940–1950) is an older bibliographic serial covering the history of technology which provided a number of important early citations. Other useful bibliographies included the ICOM publication *Bibliography of Works on the Conservation of Ethnographic Materials* (Walston and Norton 1987), and the catalog of the Tozzer Library of the Peabody Museum at Harvard University. The Tozzer Library catalog (Harvard University 1988) is a particularly useful resource for the literature of archaeology and anthropology because it lists both monographs and individual journal articles, from the early 1900s to 1988, by author and subject. The authors highly recommend this bibliographical source to ethnographic conservators as a starting point for references relating to objects in a particular cultural area.

### "Buried" Information

It is sometimes possible to determine exactly what surface an object was intended to have and how it was made. Important information bearing on this is sometimes buried or integrated into sources that may seem irrelevant or marginal to the immediate interests of conservators. An example would be the unpublished journals or letters of an artist or works that are primarily art historical in nature. By examining the writings of artists we can often find discussions of techniques used and the kind of appearance the artist was trying to achieve. A well-known example is Delacroix who was very well informed about the activities of restorers and held definite views on the treatment of his own works (Smithwick 1991). Obviously this is the case only with artists who have left written records. The importance of using this resource when it is available cannot be overemphasized.

Sometimes a society will not have written records but will be visited by cultures that do. The accounts of early travellers to a given area or those of missionaries can provide descriptions of the manufacture of objects. Anthropologists may have visited a group of people at a critical period in their contact with Western cultures and documented information now lost.

Monographs of artists produced by art historians, especially those produced to accompany exhibitions, often contain technical appendices with information about the materials used by the artist and the techniques used. Detailed analytical information and conservation treatment is often included as well. Unfortunately,

because this information is buried within its art historical context, it may often be missed when searching the literature. For example, the technical analysis of plasters and pigments present in the wall paintings at Teotihuacan (Littman 1973) is found in an appendix to *The Murals of Teotihuacan*, an art historical stylistic analysis of the murals.

For contemporary and modern art, interviews in art magazines (such as *Art Digest* and *Art News*) are a good source of information about technical matters and the artists' intent. Usually the information is not technical but in some publications, particularly in the early 1950s, there was a sort of "studio tip" mentality that was an underlying premise of some publications. More recent publications tend to contain interviews that confine themselves to the deployment of elaborate intellectual constructs. Nevertheless, they still occasionally discuss technical matters.

Finally, we contacted a number of individuals who had expressed an interest in the topic or related topics. Many of them maintained bibliographies for their own use or for distribution to students. It is always useful to consult individuals who have developed expertise on a topic and gained a familiarity with the literature. It was surprising to discover how many people were interested in the same or related topics, but in an industrial context.

### **Information Sources for the Material Culture of Non-Literate Societies**

Understanding the technology used to produce an early Netherlandish painting is a great deal easier than trying to figure out the technology used to produce a painted wooden artifact excavated at Chetro Ketl in Chaco Canyon, New Mexico. The inhabitants of Chetro Ketl left no written material describing their methods. Unfortunately, there was no Anasazi Cennino Cennini writing accounts of the types of materials and techniques used. There are primarily two options to determine what was used and how it was used: scientific analysis and a review of anthropological literature. For an extinct culture, one might look to the descendants of the people who created the artifact and use ethnographic analogy. Even after many generations, cultural practices may survive intact or virtually intact. The technology of descendants can sometimes provide valuable insights into earlier methods.

Early anthropological accounts describe methods used by Pueblo Indians in the Southwest for the gathering of pigments and the preparation of paint (Bunzel 1932). The assumption that very similar methods and materials were probably used at Chetro Ketl is not an unlikely possibility. Scientific analysis can be used to test the accuracy of our assumptions. Blind reliance on ethnographic analogy is not an acceptable procedure. However, people generally use the materials available in their immediate environment. The widespread use of non-local materials is a recent phenomenon, although some cultures of the past have used large quantities of exotic materials. Even the most seemingly isolated societies may have some sort of trade contacts. Australian Aborigines trade ocher over long distances. Ocher mines in certain locations produce a highly prized pigment that is traded over incredible distances. Nevertheless, most materials used (especially organic binding media) are local, so it becomes important to look to ethnobiology for an understanding of the resources available in a given location and how they were likely to have been used.

### **Ethnobiology & Ethnobotany**

Ethnobotany, the portion of ethnobiology dealing with plants, has an extensive literature. An immense amount of work has been done to document the plants used by various peoples and the methods used in processing the plant material. For the most part medicinal and edible plants have been the focus of these investigations, but most accounts also include information about plants used for material culture purposes. Recently, the direction of ethnobotany has changed to focus more on the interaction of groups of people with their environment in broader terms. As a result of this new focus, a comprehensive approach is



being taken that includes more information about plants used for purposes other than food and medicine.

Unfortunately, many groups of indigenous people have perished or been assimilated while these methodological changes were taking place. An immense amount of information has been lost forever and we will never know what was used to make many objects in museum collections. This situation is becoming so prevalent that ethnobotanists are shifting the focus of the studies to the "peasant" agriculturalists that have supplanted the indigenous people. These farmers rely heavily on naturally occurring plant products for a wide variety of purposes. Some of the knowledge of the previous inhabitants survives with these people.

### Organization of the Supplement

The AATA supplement consists of five sections and an introductory commentary which explains how these sections interrelate, along with a glossary. The first section is concerned with the history and technology of the manufacture and use of matte paint, and elucidates the reasons one encounters high pigment volume concentration paint on objects in various cultural and historical contexts. A following section on analysis is included because it is sometimes necessary to confirm observations or conclusions relating the technology and materials of the production of this type of paint, or because there may be a total absence of previous information. The physical and optical properties section includes references, primarily from the coatings industry, which explain why matte surfaces are light in appearance and how the physical and optical properties are affected by introduction of a consolidant. A further section on observations of deterioration and explanations of deterioration mechanisms precedes the final section on the conservation treatment of ethnographic objects and related systems, with an attempt to be a comprehensive coverage of the conservation literature from 1966 to 1992.

### Conclusion

The disappearance of human cultures and plant and animal species has created a crisis for anyone interested in the manufacture of ethnographic objects. It is already necessary to go to natural history museums to see some of the plants and animals used in manufacturing these objects. Thus, a greater urgency was felt by the authors to improve knowledge about the variety of literature from various disciplines, as well as first hand accounts. Some disciplines, such as anthropology and archaeology, almost entirely lack the sophisticated information resources found in the fields of chemistry and coatings. In order to begin to make a thorough search of these areas it was necessary to employ many strategies for finding documented information.

Preconceptions about where to find information or what search terminology to use proved to be serious pitfalls. And, although it can be very time consuming, contacting numerous specialists greatly adds to an understanding of many aspects of the nature of the problem and widens access to relevant information. This process also heightens awareness of areas where the problem occurs where previously there had been little familiarity.

Despite growing knowledge of the breadth of the problem, the focus of the bibliography has remained ethnographic objects. This is because, in addition to the great number of these objects that fill museum collections all over the world, there is disproportionately little research done on the conservation of ethnographic objects in comparison to research in support of the conservation of objects in other areas.

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## Abstract

Recording historical architectural and archaeological sites using RolleiMetric Close-Range Photogrammetry Systems. Semi metric cameras are fitted with a réseau plate in front of the film plane that imprints crosses on the film at the time of exposure. A series of intersecting views with the same points visible in three or more photographs allows the software to calculate the exact camera taking position. This data is used by the program to produce high accuracy scale drawings, or 3D models of the original object. This non stereo technique makes close range photogrammetry an economical measuring device with numerous applications for heritage documentation.

## Keywords

Semi metric cameras, multi-image orientation, architectural, archaeological, non stereo photogrammetry

# The Use of Multi-Image Close-Range Photogrammetry for Recording Historic Architectural and Archaeological Sites

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## Introduction

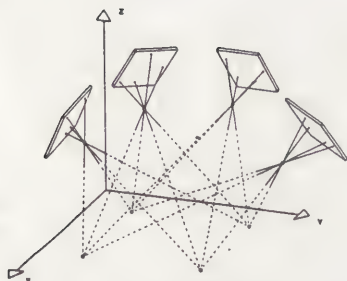
Recent research has developed a new approach to terrestrial photogrammetry. By using inexpensive PC computers and powerful software it is now possible to accurately compute the exact camera positions when photographs are taken. Unlike stereo photogrammetry a purely analytical system eliminates the need for fixed focus, beam mounted stereo cameras with little flexibility or mobility. A minimum of three converging photos are taken with a number of unambiguous points visible in all photos. The enlarged photos are taped in place on a high resolution digitizer. Then a rough sketch of the photo taking positions is digitized to determine the initial starting values. The camera lenses are supplied with all lens distortions noted in the factory calibration protocol. With multi-image orientation (See fig.1), the computer can determine the image coordinates making it possible to extrapolate and ray trace from the image coordinates through the principal point of the lens to the object. All measurements in the photos are transformed to the réseau crosses for numerical correction of image deformations. This orientation process can be repeated using the bundle adjustment program for a best fit calculation of all values (Wester Ebinghaus, 1985).

## Field Recording

By utilizing the features of a professional photographic camera, such as the RolleiMetric, on site time is very short. The ease of use combined with interchangeable lens and other accessories allow the camera to move with few restrictions. Most photographs can be taken hand held from very low or elevated viewpoints. The use of a high-lift tripod rather than a boom arm or man lift is much safer and faster. The wide range of lenses allow taking positions that would be impossible with stereo mounted equipment. By mounting a video camera pickup of the groundglass, the camera can be used in restricted locations. Architectural documentation yields its own particular requirements as many historical sites have deteriorated to the point where traditional hand measurements are unsafe to carry out. The noncontact capability of close-range photogrammetry is of importance in elevated structures that have limited or dangerous access. Due to the camera's light weight, a blimp can be used with ground control of all functions via microwave with an operating height up to 150 meters.

## Multi-Image Orientation

The process of multi-image orientation (See fig. 1) begins by taping the enlarged photos from a sequence to a high resolution digitizing tablet. Prints do not have to be any larger than  $20 \times 20\text{cm}$  as the cursor is used with a  $4\times$  magnifier to identify points. A rough sketch of the taking sequence is digitized to input the approximate taking position and attitude of the camera for each photograph. This initial information is used to determine the external orientation of the sequence. The same points in several photos are input via the digitizer and these are used by the system to calculate the camera position and the 3D coordinates of the points. The RolleiMetric MR2 Program uses the camera calibration and other information to correct for image deformations. If one imagines that the camera is used as a projector with the film image of a particular photo projected back onto the object, when the superimposed image matches perfectly the position of the camera can be measured precisely. When this method is used to position the camera for all the photographs, we can measure the distance between



\*Figure 1 Multi-Image Orientation

any points by using the multi-image orientation method to calculate the exact points on the object. External geodetic information can be included in the calculations. Accuracy of 1:2000 is easily achieved and measuring points in 3 or more photographs virtually eliminates operator error. The final step of measuring and drafting can take place directly in the Auto Cad (R.) environment. Details and measurements are input via the digitizer as a point, poly line or continuous line mode allowing intricate patterns to be traced from a single photo. The output can be used to allow drawings in either elevation, plane or any plane that is selected from 3 coordinate points. The result files can be used by other Cad programs via DXF transfer.

A typical recording session of an architectural site entails some targets to be attached to the object. An extendible pole commonly known as a "painter's pole" can be modified to allow targets to be fastened on wooden structures with simple thumb tacks. The targets are easily removed using a scraper attached to the same pole. Stone or brick structures require the targets to be fastened using latex or clear caulking compounds that can be removed without marking the object. Telescoping poles allow targets to be fastened at heights up to 10 meters and the use of extension ladders is greatly reduced or eliminated resulting in increased safety for field operators. The system requires a scale in the scene that is approximately 50% of the object size. Ideally a vertical and horizontal measurement between two points is taken. In most instances natural signalization can be used for the evaluation but targets are easier and faster to identify than a window corner or mortar joint. Recording sequences must be planned to attain optimum ray geometry by using the simple rule that a point to be measured must appear in at least 3 or more intersecting photographs. The ideal coverage of a structure should be approximately 10 meter blocks with some overlap of the photos to allow linking the photo blocks during the evaluation stage. Establishing the level of the structure can be achieved by the placing of specific targets using a construction level or if necessary a simple string bubble level to achieve known "Z" values for the object coordinates. The photographs also represent an infinite data base that eliminates forgotten field measurements and replaces regular site photography.

Archaeological sites require slightly different techniques for recording but the same principles apply. The use of multi-image recording from various viewpoints is of particular benefit when the site prevents normal high views to be taken. Previously a difficult location required an "A" frame to be rigged over the site with all the inherent potential for accidents and damaged equipment. The use of a high lift tripod and intersecting views can record the excavation with relative ease and speed thus eliminating costly down time for the digging crew. The ability to document in situ and develop a 3D model of the site with every layer shown is now possible. The time of recording an artifact by regular photography, hand measuring and drawings is reduced. Safety is a factor on underwater archaeological sites and the reduction in bottom time is a major benefit. The RolleiMetric Camera is placed in an under water housing and can be used to any depth that normal scuba divers would reach. The use of very wide angle lenses allow trenches to be recorded and stratigraphy that would take many days to measure and draw on the site are done in the comfort of an office in a matter of hours. An archaeological site that has toxic waste or other contamination dumped on it can be documented with reduced exposure time for the staff.

### Conclusion

It is now possible for close range photogrammetry to be used as a recording technique with relatively inexpensive equipment. The skill level of a Cad operator is sufficient to produce results previously obtainable only from a highly skilled photogrammetrist with the associated costs. The light weight of a 35mm RolleiMetric Camera will now allow documenting locations that would be inaccessible with large stereo cameras. Complex structures can now be recorded with a hand held camera and transferred to a computer aided drawing with relative ease.



**Materials**

Rollei Fototechnic, 196 Salzdahlumer Str., 3300 Braunschweig, Germany, 49 (5) 316800.

Prometric Technologies Inc., 5080 Singleton Drive, Hilliard, Ohio 43026, U.S.A., (614) 777-5757.

Prometric Technologies Inc., 250 Don Park Road, Unit #3, Markham, Ontario, Canada L3R 2V1, (416) 474-9837.

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## Abstract

This article is the first description of KONREG, the Danish National Museum's largest and most complex database system. The purpose of KONREG is to aid the Conservation Department. KONREG consists of an administrative section to keep track of the objects being conserved, a budgeting system to estimate and control the resources used to do conservation, and a system to record the various stages of conservation of an object. Help is provided by easy access to global indexes containing infrastructural data such as lists of materials and standardised treatment sequences. These stored standards and indexes are dynamically developed, giving rise to an interesting possibility: that standards for a particular area can be defined gradually and on the basis of conservation as it is done in practice, rather than based on predefined standards to be rigidly adhered to by all conservators in all areas.

## Keywords

Information technology, database, practice-based standardisation

## KONREG—A Database Management System for Conservation

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## Introduction

Denmark's National Museum is a cultural historical museum with Danish collections ranging from prehistory to contemporary times. It also has several special collections, for example a very large ethnographic collection, and collections from the classical Mediterranean cultures.

In addition to its own collections, the National Museum has duties concerning the rest of Denmark including maintenance of churches and profane buildings, monuments, and conservation work for other museums and private persons. The Conservation Department at the National Museum is thus Denmark's largest, with conservators educated in all conservation areas, and with research responsibilities.

In 1988 the Conservation Department decided to reorganise its administration and registration of conservation activities to use IT (Information Technology). This was carried out in cooperation with the National Museum's new Documentation Unit, established in 1987.

The Documentation Unit's task was to develop a database system to register all the museum's objects; and to support the introduction of IT in other areas, particularly in connection with the museum's research and expository activities.

Introduction of IT at the National Museum has in many ways developed differently than at most other museums. Substantial resources were allocated from the start, making it possible in only 5 years to register all the museum's large collections to form the GENREG database, which today holds data for almost 1,000,000 finds and objects.

In addition to GENREG we have developed KONREG, the Conservation Department's database project. This system, not heretofore communicated to the museum world, is nonetheless the largest database system ever realized at the National Museum.

Another exceptional aspect is that nearly all system development for the National Museum's projects has been done by the museum's own staff with a minimum of external consultancy. Especially noteworthy is that conservators with special interests in IT have participated actively with the Documentation Unit in the analysis, design, and implementation of the KONREG system. The importance of this has become evident in the working out of standards for the conservation part of the system.

Finally it must be mentioned that there have been resources enough for the National Museum's IT projects to follow, both theoretically and technically, the rapid development of IT in general. This has both positive and negative aspects as we today, only 5 years after the Documentation Unit was established, are already moving away from a centralised monolithic system, and are establishing a client/server net and milieu; that only 5 year-old terminals and PCs (personal computers) are already being replaced by stronger and faster PCs with window/mouse interaction; and that new, more sophisticated, and more natural user interfaces are continually replacing older ones.

The rather comprehensive KONREG system consists of three interdependent parts: 1) an administrative section, 2) budgeting, and 3) registration of the conservation process. In the following the first two will be discussed only briefly, while registration of the conservation process will be described more completely.



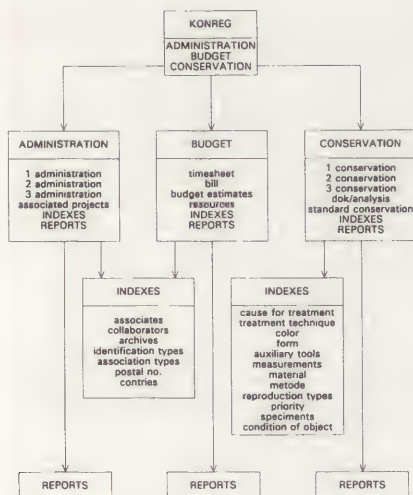


Fig. 1: System overview.

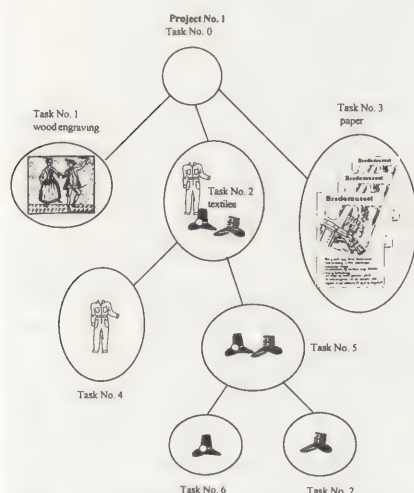


Fig. 2: Hierarchical division of project into subtasks.

The system overview (fig. 1) shows menu and registration screen images. From every screen image the user can obtain online help, and may also access central indexes—tables containing infrastructural data used throughout KONREG.

## Administration and Budgeting

KONREG's administrative part encompasses case planning, identification of the object(s) to be treated, and estimation of the resources needed to carry out the conservation task.

### Planning the conservation project

Conservation projects include church restorations, individual objects, larger collections of objects, and research investigations, just to mention some typical ones. Most projects will naturally be subdivided into several subtasks whose kind and number are not always evident at the time the project is first planned. It is thus possible continually to register a project's development and dynamically to decide its division into subtasks without limitations.

A project is divided into subtasks in a hierarchical manner, as indicated by fig. 2.

One should whenever possible plan a project so as to ease later registrations during the conservation process. For example, one can group the objects in a task into subtasks so as to register the conservation process only once for all objects to be treated in the same way. For instance, all wooden, iron, and bronze objects in a certain conservation task can be put into three subtasks, but it is of course also possible to register a more complicated conservation process for any individual object. For example, one can imagine that an altar panel is divided into paintings, woodwork, and metal parts, each to be handled separately.

A project can also be planned along entirely different dimensions. For example one might wish to emphasize budget planning. If an exhibition requires treating many different types of objects before the exhibition, one may wish to establish a common budget for all the objects, or for groups of them.

### Object identification

Since the Conservation Department receives tasks from many sources, it is essential to solve the problem of object identification. One reason for electronically registering conservation information in the first place is to be able to recall objects for further conservation, either after a fixed amount of time has elapsed, or if one discovers that a certain conservation method or material has undesirable effects.

Museum objects are mostly well-documented and identifiable through the museum's registration system. On the other hand many objects come to the Conservation Department directly from an archeological excavation with only an excavation number. This is not necessarily the same code the museum will use for long-term identification.

Non-museum objects can be still harder to identify. A fresco can of course be connected with the building wherein it is found, but may need further identification through its placement in the building and perhaps also through its theme. Objects belonging to private persons are nearly impossible to identify perfectly, but one can begin by identifying the owner, if this is allowed, and by describing the object itself.

Given that object identification can be so varied, it is impossible to determine in advance just how a particular object is to be identified. The KONREG system thus allows the registrar himself or herself to choose relevant identification types and combinations of these.

### Budget planning

Part of the KONREG system aids budget planning, estimating the number of hours a given conservation task will require. The estimated amount can con-

tinuously be compared with the number of hours actually used. The latter is delivered to the accounting part of KONREG via monthly reports.

Given this information, one may calculate how many new tasks can be started at any given time. Such resource calculations are quite important in an organization of this size—in order to deliver a given product at an agreed time, to utilise staff resources effectively, and to be able to ensure that conservators have sufficiently long undisturbed periods to do research.

### KONREG'S Conservation Part

We will describe KONREG's conservation part more fully, but detailed descriptions are beyond the scope of this article. The conservation part comprises primarily:

- 1 Registration of a conservation process
- 2 Registration of documentation and analysis
- 3 Definition of standard conservation processes
- 4 Infrastructural tables (indexes)

#### *Registration of a conservation process*

Three screen images are used to register a conservation process. The first two serve partly to plan the conservation process, and partly to describe the object, its materials and fabrication techniques. The third is used to register the actual conservation process.

When registration begins the project/task number is entered, and the title under which the project/task has been entered into the administrative registration will be shown. If the current task is a part of another, the number of the superior task will also be shown.

The conservator can now divide the project/task hierarchically into individual tasks whose conservation processes can be registered separately. If, for example, one is to register treatment of a chair with gilded leather upholstery, one may wish to register separately the treatment processes for the chair's wooden parts and its upholstery.

The object's actual identification is done as described above in KONREG's administrative part, and the conservation description should not of course be a repetition of information already found in the system. Nor should the conservator's description be a repetition of information already registered in KONREG's sister system GENREG (the system mentioned earlier for registering the National Museum's objects).

Since the Conservation Department receives tasks from many sources, often without comprehensive electronic registration systems, it is sometimes necessary to register some data not directly relevant to the professional side of conservation. The conservator may give more detailed descriptions of an object or its parts, e.g. age or provenance, but the main emphasis should be on describing the object's dimensions, materials, and fabrication techniques.

When registering object materials, one may record whether a material is a surface material or a fundamental material. If an object consists of many materials which are partly or completely layered, one can indicate the precise order of the collected composition of materials.

When registering the treatment of a given object, one first registers the object material's state and the reason it is to be treated. One might think that this information should instead be coupled directly to the object, but in practice there can be several different states and reasons for treatment. For example, an object can have been damaged by insects, and by moisture, and have fallen on the floor.

A given treatment may not require any special treatment material to be used—for example when an object is only to be cleaned with a brush. If one or more auxiliary materials are needed for a given treatment this can also be registered,



again without restriction on the number of materials being used in any single treatment.

For large conservation problems, the registration process quickly becomes very complicated with a risk of losing the overview. It is, however, easier to preserve an overview in an electronic system than it is to describe and explain the project in text, as is attempted here. Further, experience has shown that it is usually easier to gain an overview of a conservation process directly on the screen rather than via printouts.

#### *Registration of documentation and analysis*

With every data record (either an object description or a conservation process) it is possible to call forth a screen image to register current documentation or analysis. One can for example state that some information about a given object derives from an analysis that has been performed, and one can register all relevant photos, spectral analyses, etc. which are available as supplementary documentation of a conservation process.

#### *Definition of a standard conservation process*

New conservation methods are continually being developed, and new materials frequently come into use. Still, for shorter or longer periods one will be inclined to treat a larger number of similar objects in a uniform way. It would be pointless work to have to register the same conservation process for perhaps several thousand objects, so it is clearly advantageous to be able to register a given conservation process only once, and thereafter to have this standard inserted by machine every time an object is to be treated by the same process.

In a special screen image, nearly the same one as used to register a conservation process, one may register such standardised conservation processes.

One calls in a standardised conservation process by entering the standard's code in a special field of the screen image used to register the object's material.

Once this code has been called in, the standard's values are inserted into the registration screen image. Further, one may accept the standard as it stands, or it may be edited if the given object is to be handled partly with standard and partly with nonstandard methods. Similarly, several standards may be called in extension of one another.

The data content of standard conservation processes is stored electronically directly in connection with the individual objects. A standard can thus, if regarded as infrastructural data, be erased and edited by need, e.g., if the standard has been changed or is no longer to be used. The standard that was used at the time of registration in connection with a given object will, naturally, always be valid for that object.

#### *Infrastructural data (indexes)*

The system's most advanced way to define standards is by defining sometimes rather comprehensive standard conservation processes. In addition, nearly all fields in KONREG screen images have standard default values. For example, lists of materials have been developed specifying both naturally occurring and synthetic materials, treatment methods, auxiliary materials, and more. The system overview gives a list of the infrastructural indexes.

On-line help is available for every data field with standard control, giving the conservator searching access to its associated standard lists. If a desired standard value is not found, he or she can insert a new value, which is accepted by the system and supplied with a special code. From time to time such new standard values are scanned and, if accepted, supplied with a proper system code. Nearly all indexes are built up hierarchically, so insertion of a new value requires the conservator to know how the standard is structured.

Standards are naturally found in most conservation areas, but these are not always formally described and documented. By registering standards in KONREG one

gradually builds up a catalog containing many different types of conservation data, as standards are defined and registered. This itself is always current and, by saving older standards, one can form a historical document of the current "state of the art" within the conservation area.

Electronic systems make it possible to build standards on the basis of what actually happens in the real world, and to regard a standard as a dynamic process. In older systems (including older electronic systems) it was necessary for a standard to pre-exist before registration could be begun at all—but in the example described here, one can see that standard building can be done in a more dynamic way. Further, it is done with expert participation, namely by those who daily carry out, develop, and register conservation processes. In contrast, earlier systems imposed standards in advance, based on standardisation work done by a few experts or teams of experts. In many areas one can expect to see that standards will not be found in any fixed form, for example, in a handbook, but that a standard will rather become established "by demand", i.e. it will be built up progressively on the basis of what is actually registered.

### Conclusion

KONREG's administrative and accounting parts have been used for more than two years. In this period nearly 1,100 projects have been set up, concerning some 9,000 objects—though herein are not counted around 100,000 objects which were handled during an internal move from one National Museum location to another in connection with rebuilding.

Introduction of Information Technology has not led to organisational changes in the museum's work patterns, but IT has in many instances caused curators and conservators to see possibilities for documenting in new ways, and to register knowledge not only in the form one is accustomed to, but also indirectly in the system data structures.

Some of the most acute needs at present concern storing and making accessible pictorial material in KONREG. There is no doubt that photos, films, sequences of photos etc. will make it possible to eliminate much textual data entry completely.

We have begun to regard IT not as a necessary evil to be established once and for all, but rather as a process that can change our way of thinking. Therefore we do not believe the system we have developed up to now will satisfy our needs for a long time in the future, but that the system will be under continuous development.

This makes it necessary to follow the development of IT quite closely. The largest problem we have encountered is that system development is too slow using the tools we have had available until now, but more sophisticated tools are rapidly being developed. In particular, the applications tools we used to develop KONREG have been very demanding of programmer resources. Now that the system has functioned for two years, we already wish to extend the system's flexibility by shifting to Powerbuilder-like tools for working out new Windows applications in order to satisfy the requirements and expectations that have come up during the system's short lifetime.



# Working Group 5

Polychromed Sculpture

Sculpture polychrome





## Abstract

The devastating earthquake of 1976 caused a lot of damage to the cultural property of the Friuli Region of Italy. The church of Madonna del Giglio in Aprato di Tarcento collapsed during the earthquake, and only after several days its polychrome wooden retable was saved from the debris of the building, broken into innumerable fragments. In 1989 a research program was set out and in 1990 the conservation program began. The most difficult choice concerned the operative methodology to be applied. With the support of documents and old photographs, the constitutive elements and materials of the altar were identified and their location established, damages were assessed, and all existing fragments were analysed and graphically plotted. These studies enabled us to make a complete drawing of the altar and to start working on its structural rescue and aesthetic presentation, which is our present concern.

## Keywords

Retable, altar, polychrome sculpture, earthquake, interdisciplinary

## The Rescue of a 17th-Century Retable: Methodology and Conservation

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### Introduction

The conservation treatment of a large polychrome wooden altar of 1604 (1), heavily damaged by the earthquake of 1976, offers us the opportunity to present our general methodological approach to conservation, our intervention plan, and the present stage of development of our work. In particular, we would like to describe our method and its underlying principles rather than the technical execution of the various operations. In its operative phase, the reconstruction of the altar has involved various disciplines: conservation, history of art, photography and architecture.

### Wooden sculpture in Friuli and the altar of Madonna del Giglio

The polychrome wooden sculpture in Friuli represents not only the art, but also the history, civilisation and customs of the region; it is a product of local masters, at the same time painters, carvers or gilders. This kind of art met the practical requirements of poor people: they could not commission famous artists to decorate their churches because it would have cost too much, but still they wanted their devotional objects to have at least a rich appearance. For this reason fabulously coloured, gilded and glazed wooden altars were built to ennoble humble little churches and thus fulfil the modest expectations of local churchgoers.

The Church of Madonna del Giglio is remembered in ancient documents, as far back as the Middle Ages, as a place of popular pilgrimage. We know from mural inscriptions that its structure was modified various times, above all in the 16th and 17th centuries. The interior, divided into three aisles, was magnificently adorned by Giovanni Antonio Agostini with the high altar (See fig. 1). He was a well-known painter and carver, active from 1570 to 1631. The altar distinctly displays the transition to mature 17th century style; it represents an important turning-point in the artistic production of the time and a source of inspiration for later artists.

Sculptures of Virgin Saints and Christian martyrs, of the Virgin Mary and the Angel of the Annunciation, and of God the Father were lodged on different levels in an elaborate and very rich structure. The simple and almost massive type of altars favoured up to that time was modified to include fluted columns, a second level of niches, rich ornaments and closely denticulated cornices. Architectural connections between lateral elements and the centre were animated with a balanced plastic sense. Decorations became deeper and more articulated; dimensions tended to increase. Gold leaf, the use of which was limited in the 16th century, sparkled again among volutes, festoons, medallions, corbels, panels, shells and fretworks.

### To restore or not to restore?

The disastrous seismic events of 1976 caused the destruction of the church of Madonna del Giglio (See fig. 2). The high altar was crushed under the collapsing building and its broken pieces lay under the debris (2) for about ten days. Only the sculptures remained intact; the altar was broken into innumerable fragments (See fig. 3) seriously distorted and exposed to the elements. On May 28, 1976 the first fragments arrived at the church of S. Francesco in Udine, an emergency shelter for works of art. They were put into many cartons and there they remained for about 14 years, transferred from one place to another, in a state of total neglect. The absolute lack of identification of the fragments and the persistent negligence provoked further damage, until someone even suggested



Fig. 1 - The high altar of the Church of Madonna del Giglio by G.A. Agostini (1604) before the earthquake.





Fig. 2 - The Church destroyed by the earthquake of May 1976 and ruins of the three altars.



Fig. 3 - Fragments of the altar after the cartons were opened.

getting rid of them. In such a climate of poor interest and scepticism about the concrete possibility of restoration, the altar was undoubtedly well on its way to total destruction.

But as no inventory of the recovered fragments had ever been made, we thought that there was no reason to give up conservation without trying. Therefore, having resolved that intervention was the best solution, we put forward a proposal based on the following two fundamental principles of conservation:

- a) only the substance of a work of art must be restored;
- b) conservation must re-establish the potential unity of a work of art without producing an artistic or historic counterfeit, and without obliterating the traces of its passage through time.

The philosophical theory underlying our work took shape in trying to find the answers to the following questions:

1. The church of Madonna del Giglio is going to be rebuilt by the Italian Soprintendenza (Italian Ministry for Cultural Heritage) in the same architectural style and dimensions it had before the earthquake. What could be placed in the presbytery where the altar of G.A. Agostini once stood?
2. All sculptures had been recovered in fairly good condition. How and where could they be placed after restoration?
3. What would become of the fragments of the altar, if they were not going to be used in a restoration project?
4. Could one decide to ignore the deep intrinsic value of the fragments and destroy them?
5. Did the value of the altar justify the effort necessary for its conservation?

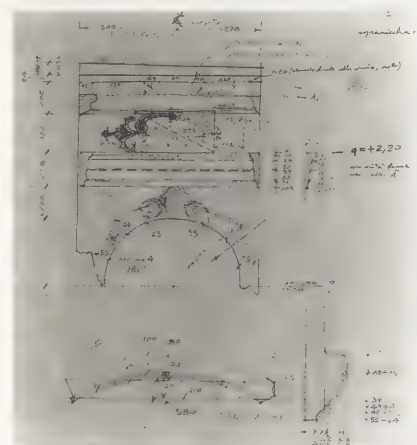
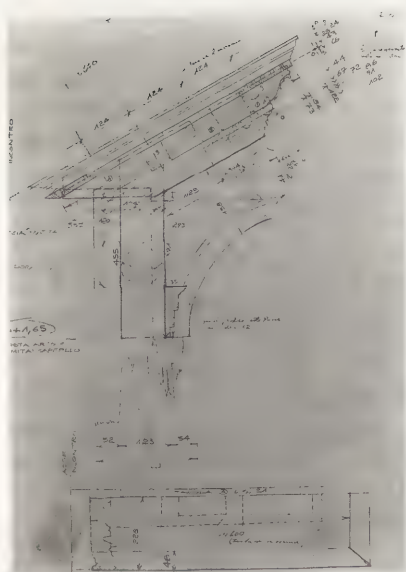
Trusting in a positive result in spite of all, our conservation project gradually took shape. We gave answers to the above questions and we worked out the following scientific-theoretical support for our applicative methodology:

1. The fundamental point is that the presbytery of the rebuilt church will need an altar, indispensable for its liturgical significance. Another important aspect is that sculptures, once hopefully restored, have to be exposed somehow. So some proposals were put forward: the exact reproduction of the old architectural frame; or a new modern altar of different shape and dimensions; or the realization of a new structure inspired by the old one. But all these solutions were neither philosophically nor philologically acceptable; moreover, each remake would have been an historic and aesthetic counterfeit—it could have served a didactic and memorial purpose, but it could never have made up for the original. For these reasons we decided to opt for the restoration of the original altar.
2. Sculptures and architecture are a whole and not a totality, i.e. a mere composition of parts; they would be senseless without the formal links imposed on them by the artist—it would be like reading the words of a poem in a dictionary, where, deprived of the unifying power of the verse, they are just groups of semantic sounds and nothing more.
3. Having accepted the idea that the work of art is a whole, and that, even when physically broken, it still continues as a potential whole in each of its fragments, we can state the following principle: any intervention aimed at recovering the original unity of a work of art, through the recovery of the potential unity of its fragments, must take into account only the indications implicit in the fragments themselves or to be found in authentic evidence of its original condition.
4. The fundamental aim in the restoration of a work of art is the recreation of its potential unity. An action of conservation is legitimate only if it can be clearly identified as to the time of its execution - conservation must not reverse time or suppress history. Consequently, in order to respect the complex historicity of a work of art, conservation must not be a secret or timeless event, but a clearly datable one.
5. Since a work of art is above all a product of human action, its appreciation should not depend on changing tastes and fashions. The fragments of a work of art, an altar in this particular case, always bear evidence of their belonging





Figs. 4–5 - First cataloguing of fragments.



Figs. 6–7 - Sketches and field measurements.

to a historical past, and their value cannot be assessed against the tastes of our times.

Ruling out the possibility of reconstruction would have meant destroying two historical values: first, the potential unity of the work of art; second, the memory of the historical event, i.e. the earthquake, that heavily marked its existence. Opting for non-intervention would have meant disregarding those who laboriously built up this altar, and those who took personal care of its maintenance, and those who prayed together with simple but deep faith in front of it, including that child who, in the afternoon of May 6, 1976, while sitting with his friends on the church benches, saw the hand of God the Father move, like an omen of the disaster that was soon to destroy so many lives.

For all these reasons we think that this altar deserves to be restored, so that the message it conveys can reach those who will come after us, a symbol of the victory of life against the destructive power of the earthquake.

### Selection and identification of fragments: methodology and practice

The only existing documentary material upon which we could base our work were the sculptures, the fragments of the altar, and some old photographs from the parish archives showing the front of the structure.

A simple proportional calculation led to a rough estimate of its dimensions: 4.5 m. high and 5 m. wide, with protrusions and recesses of variable depth.

In order to understand the function, and determine the position of each fragment for classification purposes, it was necessary to single out a method for establishing the relationships between fragments, and those between the fragments and the imaginary reassembled whole.

Adopting an interdisciplinary approach, we implemented the following procedures:

- archival survey of photographs and documents;
- photographic analysis;
- plotting of fragments;
- definition of the constitutive moduli of the altar;
- plan and level of the architectural structure of the altar;
- visual examination of the conditions of conservation;
- analysis of employed woods;
- analysis of the surface of the altar.

All fragments were placed on the floor and photographed (See figs. 3–5). The pictures were then compared with the ones from the archives. An enlargement of the old photographs was very useful to evaluate the proportions of the front, but not of the back and sides of the altar.

To avoid undifferentiated measurements of the fragments we decided to implement a selection:

- fragments of very large dimensions
- fragments of small dimensions

The first were accurately measured and plotted on a drawing with numbered sheets (See figs. 6, 7): this was absolutely necessary for the evaluation of dimensional space relations. The big fragments were then put in order on the floor. We were thus able to make a first general classification by colouring the original location of each fragment on a black and white drawing of the altar.

Wooden altars, especially those of large dimensions, were built according to precise rules of carpentry. Single elements, of limited size, were built in the “bottega” (craftman’s shop) and then transferred to their final destination to be assembled. The altar of Madonna del Giglio was also made in this way and its architectural structure was the result of the assembling of 30 different moduli:

- middle predella was labelled and plotted with the letter “A”;
- left and right predellas with arches with the letters “U” and “V”;





Figs. 8-10 - Maps of moduli "H" and "I" and plotted fragments.

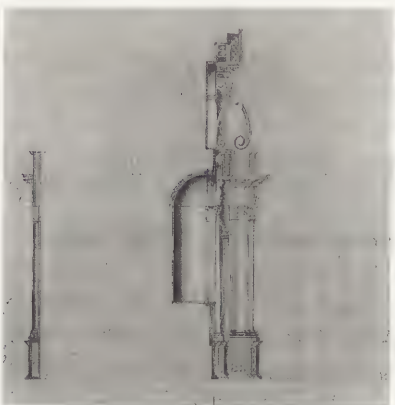


Fig. 11 - Graphite and water-colour project drawing: vertical sections.

- left column, capital, parastas, dado with panel with the letter "F", etc. (See illustrations).

All these moduli were graphically plotted in scale-drawings 1:5 in the following projections: front, side, bottom, top sections at various levels, developments of concave and convex surfaces. All these drawings were made in graphite pencil and water colour on cotton water-colour paper. A complete series of heliography copies of the original drawings (See figs. 8-10) was made. These were used to plot the fragments.

But most of the fragments were not easy to identify. So the altar was subdivided into its constitutive elements (See figs. 4, 5): cornices, capitals, niches, surfaces with "pastiglia" on plane, concave or convex panels and small decorative elements. For example, a fragment was identified as belonging to a front column, but it was hard to determine to which one of the six front columns it belonged. Using all the procedures mentioned earlier in this article, each fragment was thoroughly analysed—the quality of its wood against that of identified surrounding fragments; its polychromatic elements, i.e. gilded or coloured surfaces (3); the type of damage it had suffered: crush and break traumas, break traumas only, fairly good condition; the quantity and quality of dirt; the complementary crack lines; the presence of nails, holes and traces of old dried glues; location and quality of overpaintings.

We decided to adopt a strictly philological approach, so that our work could develop according to the previously fixed deontological rules. In this way a very high percentage of fragments belonging to the high altar of Madonna del Giglio were clearly identified; for only 1.5% of the fragments, belonging to the back, identification, and consequently restoration, was impossible.

Every time a fragment was identified, we proceeded to mark its position on a big plan of the altar. Each fragment was classified using a letter followed by an Arabic numeral which defined its position inside its own modulus. On the plan (See figs. 8-10) the fragment was drawn in a heavy outline and was coloured in gold yellow to indicate the presence of ground, gilded surfaces or polychrome (even though partially damaged), and blue to indicate the presence of the original support but the absolute lack of ground or polychrome.

These documentary plans were essential to identify the precise location of each fragment. At the end of this stage we had drawn 9 plans with 382 fragments. An imaginary assembly of the constitutive moduli led to the conclusion that up to 80% of the architectural frame could be rebuilt.

The plans of the moduli were used to produce water-colour drawings of the altar: front and back views, plans, and sections in plane and vertical. These drawings proved indispensable when we decided to carry out the project (See figs. 11, 12).

### Restoration of fragments

When the church collapsed, most of the wooden supports of the altar collapsed with it. It was therefore necessary to place the fragments on a temporary holding structure. Before that, however, it was necessary to restore them. Craquelure, detachment and loss of surface also occurred as a result of the movements the wood suffered because of extensive thermohygrometrical variations (4). All surfaces were affected by rubble, sand and mud embedded in gesso and glue of wet ground; they also had thick layers of dirt and old oxidized varnishes, especially on small canvas paintings of predella and trabeations. In addition, there were many layers of black grease and spots of wax from candles. The altar of Madonna del Giglio had not undergone any routine maintenance or restoration after 1904, the date of the last major restoration.

Fir and poplar for carpentry, and lime for carving, were damaged by worm attacks, which in some places resulted in a sponge-like appearance. A general conservation procedure was carried out, then the surfaces were brushed and the wood cleaned with sponges.

Gilded or polychromed surfaces and ground were heavily affected by debris and



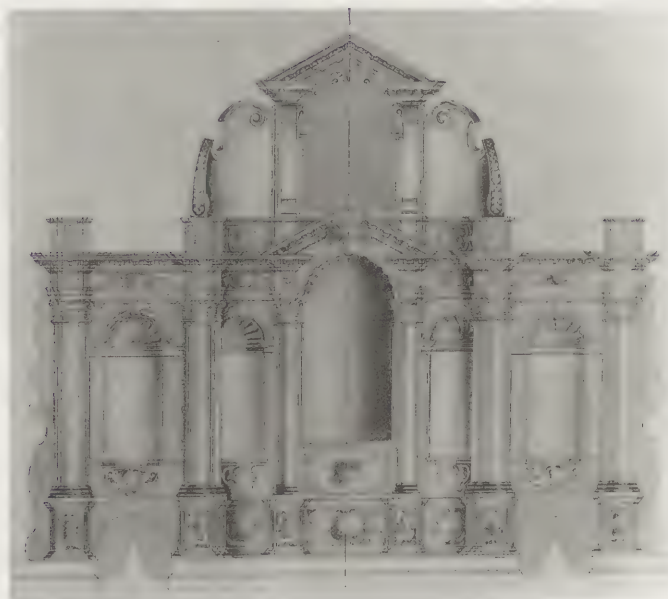


Fig. 12 - The whole altar: front.

mud. We worked on cleaning and consolidating surfaces and ground at the same time, fixing flakes with Polyvinylalcohol. On softened surfaces a mechanical cleaning procedure was carried out with in following sequence: softening, consolidation and drying. We used Lapin glue, sometimes adding a drop of vinylic or acrylic glue to fix large flakes and the pastiglia decorations. We used mixtures of non-polar solvents to clean dirt, oxidized varnish and lamp-blackened layers.

All fixed and cleaned fragments underwent deep consolidation and disinfection against wood worms with Paraloid B72 in Diluente Nitro and Permetar (wormkiller). We built a series of solvent-proof tanks, 10 cm. high and of different sizes, where the fragments were put for the necessary time in a solution of progressively variable concentration (Paraloid B72 from 3% to a maximum of 12%, Permetar 3% in Diluente Nitro). They were then put into semi-permeable bags to allow the solvent to evaporate slowly.

Following the plans and project drawings, all contiguous fragments were joined to re-establish each modulus or its significant component. Sverzature (5) and coupling of new materials was avoided in favour of maximum use of the original wood. Following the crack lines, the join was made with wooden pins, sometimes reinforced with brass screws; for temporary joins, wooden or brass bridges were also used.

At this point we felt it was absolutely necessary to rebuild in real space what we had saved until then. This operation would allow us to confirm our findings, to have a real image of the situation, to know what kind of reconstruction was best, and how to make up for lost parts and treat surfaces. In short, to have the altar speak for itself.

So a temporary holding structure, i.e. a grid of wooden beams and boards, was made in order to support the large and small parts of the altar (See fig. 13).

At the end of this phase, the size and dimensions of the altar were clearly visible: it was 4.25 m. high and 5.25 m. wide, with a maximum depth of 1.5 m. and sinuous protrusions and indentations.

Had we failed to restore this altar, we would have lost, because of negligence and the earthquake, a precious testimony of the historical devotional art of Friuli.

### Conclusion

A complete report on the work on the altar of Madonna del Giglio will be drawn up in the near future. It will focus on the complex procedure involved

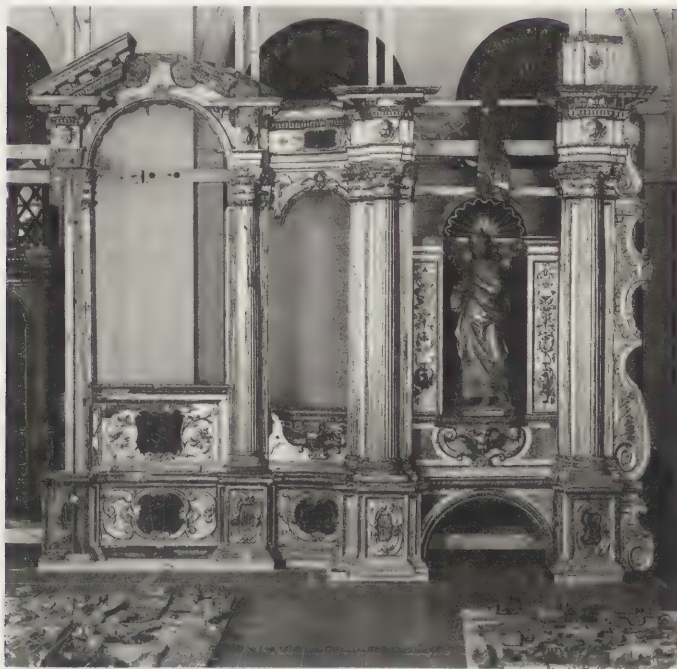


Fig. 13 - Restored fragments on the temporary holding structure: first phases of the positioning.

in the practical reconstruction of the missing parts of the altar, on the choice of methodology, materials, and finish for the surfaces. Every effort will be made to respect the surviving parts of the altar.

Historic and artistic knowledge, analysis of documents and photographs, graphic plotting and drawing, knowledge of techniques and ancient materials, technological and operative skills in conservation work - all these were necessary to carry out this rescue operation, surely not easy, but no doubt satisfactory.

We hope that this contribution will be a positive example, and will encourage others to operate with sound professional ethics on "impossible" restorations as well.

### Acknowledgements

The authors wish to thank Mons. Francesco Frezza, Priest of Tarcento, Dr. Massimo Bonelli, Art Historian of the Italian Soprintendenza, Mr. Renato Portolan for his co-operation in the restoration work until 1992 and arch. Antonio Majer.

### References

1. G. Marchetti, G. Nicoletti, *La scultura lignea in Friuli* (Milano, 1956).
2. C. Brandi, *Teoria del restauro* (Torino, 1977).

### Notes

1. The altar had two recognizable and datable restorations: 1887 and 1904.
2. Inside the Church of Madonna del Giglio there were three wooden retables dedicated to Madonna del Giglio -the high one-, S. Antonio and S. Rocco.
3. The altar showed the existence of three kinds of gilded surfaces: gold leaf on bolo applied and polished in the traditional way, unpolished gold leaf on missione and oro on conchiglia.
4. All fragments and sculptures remained under the debris and rain for about ten days.
5. Sverzature: junction of cracks by removing original wood, creating a triangular shape lodging and inserting small pieces of new triangular-shaped wood.



## Résumé

Une grande partie des sculptures de bois polychrome en Bretagne est conservée dans des édifices religieux en granit. Les conditions de conservation de ce patrimoine vivant entraînent souvent une dégradation importante de la base des objets, altérant le maintien et la verticalité des sculptures. A travers l'étude de trois cas, les auteurs proposent quelques solutions à ce problème important pour la conservation et la lisibilité des objets. Matériaux de soutien, techniques d'accrochage, possibilité d'interfaces, limites de l'intervention sont décrits et discutés.

## Mots clefs

Bois polychrome, traitement

## Problèmes de bases.

### Stabilité et verticalité de la statuaire religieuse

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## Introduction

Le patrimoine breton est particulièrement riche dans le domaine de la statuaire; c'est ainsi qu'à ce jour plus de 3500 sculptures sont protégées en Bretagne, conservées au sein de collections de musées ou bénéficiant du titre de "Monument Historique". Majoritairement d'origine religieuse, c'est aussi un patrimoine vivant, utilisé pendant les fêtes ou objet de prières quotidiennes, et une grande partie de ces objets, près de 80%, est conservée en place, dans les églises et chapelles.

C'est dans ce contexte que s'est créé, à l'instigation d'une association de conservateurs de musées de Bretagne (BUHEZ-VIE), l'Atelier Régional de Restauration. Agréé par le Ministère de la Culture (Directions des Musées de France et des Monuments Historiques), il a pour vocation la conservation du patrimoine de sculptures polychromes. Répondant aux conditions et aux besoins locaux, il est souvent confronté au problème de la stabilité des sculptures en bois.

## La conservation des bois polychromes en Bretagne

### *Le climat*

La proximité de l'Océan Atlantique assure à la Bretagne un climat doux et humide. La pluviosité moyenne est répartie tout au long de l'année et l'amplitude thermique est faible (10–15°C). Domaine forestier: chêne et chataignier.

Ce climat, ainsi que la conservation dans des édifices de granit, concourent à assurer tout au long de l'année dans l'environnement des objets, une humidité relative et une température suffisantes, voire idéales, pour le développement des micro-organismes. Même si l'humidité relative est élevée, les variations peuvent être importantes dans des zones recevant la lumière du soleil, ou en période d'averses, favorisant le jeu du bois (variation possible sur 2–3 jours de 50 à 90% d'HR).

### *Le problème*

Les sculptures sont affectées dans leur totalité, mais principalement à la base où existe un milieu confiné, humide et froid, au contact de la pierre. La statuaire religieuse conservée dans les musées bénéficie de meilleures conditions de conservation, mais présente le même type de dégâts, apparus avant l'insertion des sculptures dans les collections muséales. Ainsi la plupart des sculptures qui arrivent pour traitement à l'atelier sont extrêmement instables ou ont complètement perdu leur assise.

L'importance de notre intervention dépend en partie du lieu de conservation. Dans un contexte muséal, une restauration réduite est possible grâce à la présence d'un personnel de surveillance et de structures de protection. Ceci n'est pas le cas des sculptures conservées in situ. Elles font souvent partie de la décoration de chapelles peu fréquentées, ou seulement par les paroissiens qui les considèrent comme du mobilier et parfois comme du mobilier leur appartenant. Les micro-organismes, mais aussi les souris, les pigeons, les fêtes paroissiales sont à craindre. Les mesures de conservation préventives sont limitées à l'existence du toit de la chapelle, et le personnel communal préfère parfois protéger le matériel de sonorisation ou les bancs de la chapelle plutôt que les sculptures. En ce sens, si les conseils des restaurateurs sont écoutés, ils ne sont pas forcément pris au sérieux.

\* Auteur à qui la correspondance devrait être adressée.

Nous tenons donc compte du lieu de conservation. Cependant pour décider de l'importance de l'intervention, on aurait tort d'exagérer la différence des deux situations. Premièrement les conditions de conservation dans les structures muséales, si elles sont meilleures que dans les chapelles, ne sont pas forcément optimales. Deuxièmement, l'instabilité d'une sculpture du point de vue de la conservation préventive représente un danger réel même dans une vitrine de musée. Ainsi on retrouve la trace de la chute des objets dans les éléments arrachés et manquants; extrémités, accessoires, membres, attributs ont souvent été remplacés. Troisièmement, la plupart des sculptures représentent des saints en pied. Il est nécessaire pour leur lisibilité de les exposer debout, ceci nous obligeant à intervenir à cette fin quelque soit le lieu de conservation.

Notre but est donc toujours de redonner à la sculpture une stabilité mécanique. Si nous avons à l'esprit les principes d'intervention minimum et de réversibilité, il nous faut parfois les adapter à une situation de survie pour l'objet. En effet, les objets exposés dans les chapelles font partie de la vie religieuse et il n'est pas souhaitable de les retirer de leur contexte. Or celui-ci ne peut être changé pour l'instant. Nos limites sont aussi d'ordre financier.

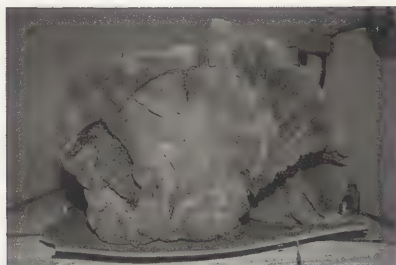


Fig. 1: Saint-Antoine. Base vue de dessous, avant restauration.



Fig. 2: Saint-Jean-Baptiste. Base vue de dessous, après enlèvement des planches.

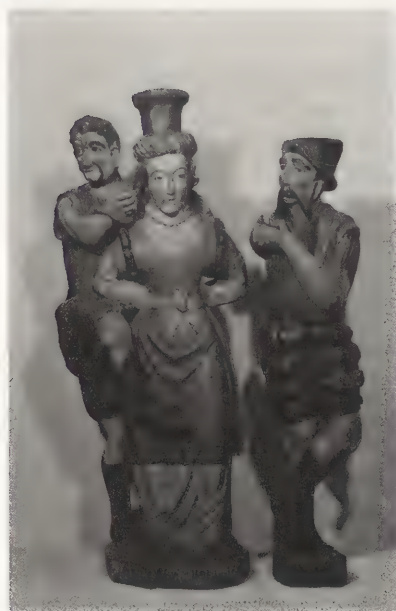


Fig. 3: Sainte-Apolline et ses bourreaux, bois polychrome, Bretagne, 2ème moitié du XVIème Siècle. Après restauration.

### Altérations et éléments de solutions

#### *Description des altérations de la base des objets*

L'activité des micro-organismes et le jeu du bois dans les conditions décrites ci-dessus provoquent une importante altération de la base des objets.

Les sculptures non évidées présentent parfois des bases convexes, permettant une oscillation de la sculpture en cas de pression ou de choc même faibles. Cette déformation concentre aussi le poids important de la sculpture (chêne massif, grandes dimensions) sur une petite zone de contact avec le sol (voir fig. 1, 12, 13).

La perte de matière, -réduction du bois au squelette lignifié ou chute de gros morceaux (voir fig. 1, 4)-, entraîne une réduction de la surface de la base ou une extrême fragilité du matériau. La base devient inapte à supporter le poids de la sculpture, elle s'écrase ou se casse. Le centre de gravité passe à l'extérieur de la base; la sculpture doit alors être appuyée contre un mur ou couchée sur le sol. La dégradation s'étend à ces points de contact avec la pierre.

La déformation ou la perte de matière, en déséquilibrant la sculpture peuvent provoquer la rupture des assemblages.

Ces altérations se sont renouvelées au cours des siècles, donnant lieu à des restaurations qui se sont elles aussi dégradées. En effet, l'adjonction de clous qui rouillent très vite dans ce milieu salin, de plâtre, de planches de bois, n'a pas enrayé le processus (voir fig. 2).

#### *Une mesure générale: l'interface de liège*

Pour prévenir le contact avec la pierre et réduire à la fois l'humidité et l'abrasion d'un bois déjà fragilisé, une semelle de liège aggloméré est utilisée comme interface, découpée à la forme de la base. Peu épaisse et d'un ton s'harmonisant avec le bois, elle est acceptable d'un point de vue esthétique et bien vécue par le public. Ce liège peut être installé par les responsables locaux car il est facile à obtenir et bon marché. Le liège est résistant mécaniquement et peu sensible aux micro-organismes; il remplit correctement son rôle de barrière. Pourtant en l'absence de données sur la colle présente dans le matériau, ses produits de dégradation ou d'autres additifs, nous ne pouvons pas évaluer l'innocuité à long terme de cette pratique. Une recherche est commencée sur ce sujet, auprès des fournisseurs et des industriels.

#### *Un système efficace: la cale*

Par "cale", nous entendons l'ajout d'un élément à la base de l'objet, quelque soit sa matière ou son système d'accrochage. Le but est de compenser la perte de matière subie par la base, de stabiliser l'objet et de lui rendre une station verticale correcte. La solution choisie doit assurer un bon soutien, c'est-à-dire,



d'abord faire preuve d'une grande adaptabilité à la forme, afin de répartir le poids et d'assurer un accrochage correct, ensuite d'une grande résistance mécanique, ne pas se déformer ou se fissurer, enfin d'une bonne résistance aux micro-organismes, car le milieu est agressif. L'accrochage, le vieillissement et la réversibilité doivent être également satisfaisants. Il faut par ailleurs un accrochage réversible car les conditions de conservation sont mauvaises et l'intervention vouée au renouvellement.

### Trois études de cas

#### *Etude de cas 1: Le bourreau de Sainte-Apolline*

La sculpture de Sainte-Apolline et ses bourreaux (1) est constituée de deux blocs: Sainte-Apolline et le bourreau de droite d'une part, le bourreau de gauche, d'autre part (voir fig. 3). Les bases de ces sculptures présentent des attaques très importantes d'insectes avec disparition de la structure fibreuse et perte de matière (voir fig. 4). La base du bourreau isolé est extrêmement réduite (hauteur de la sculpture: 160 cm, diamètre de la base: 25 cm). Elle a été anciennement consolidée avec du plâtre. Celui-ci s'est cassé et n'assure plus la stabilité de l'objet.

Après enlèvement de la semelle de plâtre, le bois est consolidé au Paraloid B72 à 10 % dans du Xylène afin de renforcer le squelette de bois restant. On choisit alors de réaliser un système de trois cales de différentes hauteurs (voir fig. 4). La cale avant, de petites dimensions, est réalisée à l'aide d'un mélange de poudre de bois et de colle blanche (constituant principal: acétate de polyvinyl). L'accrochage du mélange dans la structure lacunaire de la base est bon, le PVA formant un film très fin (2), en diffusant légèrement dans le matériau. Ce mélange est facile à obtenir, bon marché et adaptable, en faisant varier les proportions et les qualités des éléments (viscosité et concentration du PVA, grosseur de la poudre de bois) (3). L'utilisation de cette méthode est limitée par le volume, la cohérence du mélange n'étant pas très grande.

Pour les deux autres cales, hautes, on a recours à la résine epoxy SV et HV 427 Araldite (R). Cette résine est en effet, dans notre cas, assez solide pour prendre en charge la quasi-totalité du poids de la sculpture sans apparition de fissure ou d'effet de cisaillement. La mise en forme est facile, mais pour de grandes quantités de résine, il est nécessaire de procéder en plusieurs fois car elle a tendance à couler. Stable et insensible aux microorganismes, on peut la sculpter. Cependant, elle demande une mise en teinte car elle est très sombre. Comme elle réalise avec les autres matériaux un accrochage très fort et irréversible, il est nécessaire d'introduire un interface pour améliorer la réversibilité. Dans ce cas, nous avons employé le mélange de poudre de bois et PVA, bien que nous soyons conscient des limites de la réversibilité de l'opération dans ce bois très vermoulu.

L'objet après traitement tient debout, mais il reste facilement déstabilisable en raison de l'étroitesse de la base. Nous pensons en accord avec le conservateur que cette stabilisation est suffisante dans des conditions muséales. Fallait-il augmenter la surface des cales pour répartir le poids de façon à préserver le bois fragilisé ou fallait-il augmenter la surface de la base pour assurer une meilleure stabilité? Ces deux questions, de même que le traitement illusionniste de l'intervention, posent le problème d'une reconstruction du volume de la base, volume hypothétique dont nous ne connaissons ni la forme, ni les limites.

#### *Étude de cas 2: Saint-Jean-Baptiste*

La base de ce Saint-Jean-baptiste (4) a une histoire complexe. Une attaque d'insectes et de moisissures a demandé, lors du premier repeint, le remplacement de la partie gauche du socle, y compris le pied (voir fig. 2, 6). La pièce rajoutée pour former la base (environ la moitié) a été assemblée par deux faux-tenons. Comme cette pièce est débitée tangentielle, l'assemblage a tendance à fendre la pièce en deux. Un nouveau pied gauche aussi a été collé et cloué. Cet assemblage, vraisemblablement déstabilisé par le jeu du bois, a cassé au niveau des faux-tenons, avant le troisième repeint. Le socle a alors été doublé de trois planches de bois blanc (voir fig. 7, 8), clouées (18 clous). Les manques ont été bouchés avec du plâtre. Depuis cette intervention, la base a joué de nouveau, le

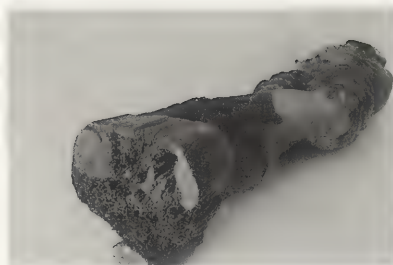
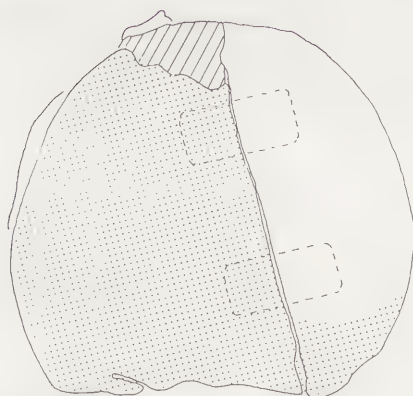


Fig. 4: Le bourreau de Sainte-Apolline. Base vue de dessous, après restauration.



Fig. 5: Saint-Jean-Baptiste, bois polychrome, Bretagne, XVIIIème siècle (?). Avant restauration.





Attaques d'insectes

Faux-tenon

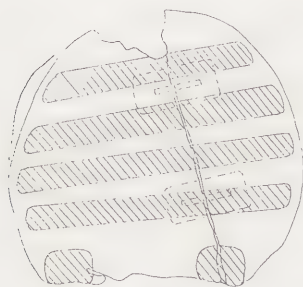
Bouchage au plâtre

Fig. 6: Saint-Jean-Baptiste. Base vue de dessous, altérations et schéma d'assemblage.



• clou

Fig. 7: Saint-Jean Baptiste. Base vue de dessous, avant restauration.



Mélange de poudre de bois et de PVA

Chevilles en aluminium

Fig. 9: Saint-Jean-Baptiste. Base vue de dessous, schéma d'assemblage, après restauration.

bouchage de plâtre a cassé, et les clous ont rouillé. Le pied gauche n'est plus en position anatomique et la base n'assure plus sa fonction.

Le problème était d'assurer la cohésion des différentes pièces de la base tout en supprimant le bras de levier dû à la différence d'épaisseur entre les deux pièces principales. Les éléments ont été démontés et les matériaux dangereux (plâtre, clous rouillés), supprimés. Les faux-tenons ont été réutilisés pour un nouveau chevillage (voir fig. 9). Celui-ci a été réalisé en aluminium afin de minimiser le jeu dans l'assemblage (chaque cheville est un cylindre plein en aluminium d'un diamètre de 8 mm, une cheville est positionnée au centre de chaque faux-tenon). Les pièces (les deux éléments de base, les deux faux-tenons, les deux chevilles) ont alors été collées à l'aide de PVA, et l'intervalle entre les deux pièces principales a été comblé avec le mélange de bois et PVA. Ce rebouchage était nécessaire pour rendre à la base la cohérence indispensable à sa fonction. Et c'est l'un des avantages du mélange poudre de bois et PVA que d'être adaptable à la forme des lacunes. Cette nécessité nous renvoie au problème plus large du comblement des fissures qui a été très bien traité par ailleurs. Suivant les conclusions de ces études, nous utilisons le plus possible le bois de balsa (5). Dans des formes



Fig. 8: Saint-Jean-Baptiste. Base vue de dessus, avant restauration.

compliquées, nous conservons le mélange poudre bois et PVA, notre budget ne nous ayant pas encore permis d'expérimenter les micro-billes préconisées dans ces travaux. Le bras de levier a été supprimé par l'adjonction de quatre bandes parallèles de pâte de poudre de bois et PVA, perpendiculaires à la surface de contact entre les deux moitiés de la base dont elles assurent la planéité (voir fig. 9). Le rééquilibrage de l'ensemble de la sculpture, la tenue correcte du personnage, a été obtenue par l'adjonction de deux talonnettes en pâte de poudre de bois et PVA à l'arrière (voir fig. 9, 10). La base des talonnettes et les quatre bandes sont dans le même plan. Pour réajuster le pied gauche en place, on a été obligé de supprimer de la matière au niveau de la cheville et d'en ajouter (feuillets de bois de balsa) au niveau de la plante du pied. La sculpture est ainsi redevenue stable et lisible.

### Etude de cas 3: Saint-Antoine

Cette représentation de Saint-Antoine (6) a été exécutée dans un tronc de chêne. Le centre du tronc correspond à peu près au centre de la sculpture (voir fig. 11, 13). La base est proche des racines et la surface révèle des noeuds importants. Cette sculpture en plein a beaucoup joué. Il existe un réseau de fissures le long du fil, suivant les cernes du bois et à partir des noeuds. La base est déformée de façon convexe et une partie importante correspondant au départ d'une racine, s'est détachée suivant les cernes de croissance, avec l'aide des insectes (voir fig. 1, 12, 13). La cavité ainsi formée a été comblée de bouse de vache, ce qui a accru l'activité des micro-organismes. Le bois, à la base et dans la cavité, est fragilisé par les insectes. Un autre fragment menace de se détacher. Sur cette base convexe et réduite, la sculpture oscille à la moindre pression.





Fig. 10: Saint-Jean-Baptiste. Base vue de dos, après restauration.



Fig. 11: Saint-Antoine. Chêne polychrome, Bretagne, XVIIème Siècle (?). Après restauration.







-  Attaques d'insectes
-  Manques
-  Cernes de croissances
-  Fissures

Fig. 12: Saint-Antoine. Base vue de dessous, altérations.

Pour la restauration de la base, on devait tenir compte de trois données: l'importance du manque, la fragilité des surfaces d'accrochage et le poids très important de la sculpture. Pour assurer l'équilibre de la sculpture, il fut envisagé de compléter la surface de la base en ajoutant de la matière. Il est par exemple possible de réaliser des semelles avec des lattes de balsa collées au PVA. Mais bien que parfaitement réversible, et optiquement satisfaisante, cette méthode n'est valable que pour des objets légers. Même avec un autre matériau, le bras de levier qui se serait exercé, aurait été très grand, les points d'accrochage étant trop peu nombreux ou trop éloignés de la base. De plus les bords de la sculpture sont fragiles, minces ou dégradés.

D'autre part, le manque était suffisamment important pour gêner la lisibilité de l'objet. Il donnait l'impression désagréable (et pas tout à fait fausse) que la sculpture était sur le point de tomber. On envisagea alors de fabriquer un volume en époxy que l'on pourrait introduire dans la cavité et qui assurerait l'équilibrage de l'objet. Mais du point de vue de la prévention, toute cale mobile mise sous un objet dans une église est appelée à disparaître. Il fallait donc une intervention solidaire de l'objet. Or la surface intérieure était fragilisée par les insectes, si torturée et d'un accès si malaisé que le résultat d'un collage était difficile à prévoir.

On pensa alors combler la cavité, augmentant ainsi la surface de portage de l'objet et la surface d'accrochage de la cale, et restaurant la lisibilité du volume. Seule la résine époxy pouvait résister au poids de la sculpture sans se déformer ou se tasser. On retrouvait le problème plus général du comblement des fissures. Dans des conditions climatiques changeantes, l'introduction d'un matériau trop dur dans le bois pouvait non seulement agrandir la cavité mais aussi étendre le réseau de fissures déjà important. Cette opération dangereuse eut été de plus absolument irréversible.

La géométrie de la cavité permettait l'accrochage d'un volume par simple verrouillage mécanique. On pouvait introduire une résine molle qui une fois durcie restait en place sans qu'un accrochage au niveau des surfaces ne soit nécessaire. On choisit donc de tapisser la cavité d'une feuille de mousse de polyéthylène puis de combler la cavité de résine époxy (voir fig. 14, 15, 16). La feuille de mousse de polyéthylène s'adaptait imparfaitement à la surface torturée de la cavité, mais suffisamment pour rendre l'opération possible.

L'introduction de cet interface avait plusieurs avantages: 1. cela évitait tout contact et tout accrochage entre le bois et la résine; 2. l'épaisseur de la feuille de mousse de polyéthylène et sa souplesse, ainsi que les petites cavités laissées entre la mousse et le bois, permettaient le jeu du bois.

Par cette méthode, mousse de polyéthylène et résine époxy, on pouvait réaliser la restauration du volume, l'équilibrage de la sculpture avec une cale fixe, l'amortissement du jeu du bois et la réversibilité de l'opération.

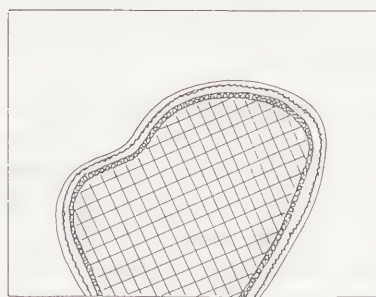
Cette méthode avait un inconvénient: la condensation possible sur la surface de polyéthylène au contact du bois. On décida donc d'ajouter un intermédiaire; une feuille de Melinex (R) (téréphtalate de polyéthylène) perméable à la vapeur d'eau mais pas à l'eau liquide, en espérant que la condensation se produise plutôt entre les deux feuilles plastiques qu'entre le bois et le Melinex (7). Le Melinex et la résine époxy débordent sous la base pour en restaurer la planéité.

### Conclusion

La conservation des sculptures in situ peut sembler peu souhaitable du point de vue du matériau. Pourtant dans ce pays de foi catholique, la vénération des images joue un rôle important dans les activités quotidiennes et la cohésion du tissu social. Ce riche patrimoine est aussi un des atouts touristiques majeurs de la Bretagne. Les Pardons, processions annuelles avec sortie des images et festivités, sont des événements religieux et conviviaux. Conserver le patrimoine est, dans notre cas, un compromis entre assurer la perennité des biens matériels et celle de la persistance des coutumes. A long terme, il passe par la responsabilisation de la population.



Fig. 13: Saint-Antoine. Vue de dos, altérations.







-  Bois
-  Résine époxy
-  Mousse de polyéthylène
-  Feuille de Melinex (R)

Fig. 14: Saint-Antoine. Schéma d'ac-crochage de la cale.

## Matériaux

Acétate de polyvinyl. Pattex bois (R), Henkel France S.A., 92100 Boulogne, France, tél. 1.46.84.90.00, Viscosité = 2500 à 3000 mPa/s.

Résine epoxy. Araldite (R) SV et HV 457, Ciba-Geigy.

Film de téréphtalate de polyéthylène. Melinex (R), Hoechst.

Liège. Liège aggloméré en rouleau, Ets. Lattière Landouzy, 59113 Seclin, France, tél. 20.32.73.32.

## Notes et Références

### 1. Sainte-Apolline et ses bourreaux

Lieu de conservation: Musée Départemental Breton, Quimper, Finistère, France. N° d'inv.: MDB 923-1-5-1. Auteur inconnu.

Date d'exécution: 2ème moitié du XVIème Siècle. Matériaux: bois (essence non déterminée), polychromie. Dimensions du groupe: hauteur: 160 cm, largeur: 80 cm profondeur: 25 cm.

Sainte-Apolline, vierge d'Alexandrie, fut martyrisée par la populace car elle refusait d'abjurer le christianisme et adorer les idoles. Elle fut frappée sur la bouche à coup de pierres et perdit ainsi ses dents. Selon une légende postérieure, un bourreau lui aurait arraché toutes les dents une à une avec des tenailles.

2. Si le PVA n'a pas une grande cohérence interne, il réalise un très bon accrochage avec les autres matériaux, d'où la solidité des films fins.

3. La résistance du mélange aux moisissures est à l'étude. L'essence du bois et différents PVA sont testés.

### 4. Saint-Jean-Baptiste

Lieu de conservation: église paroissiale de Monterblanc, Morbihan, France. Auteur inconnu.

Date d'exécution inconnue, probablement XVIIIème Siècle. Matériaux: bois de feuillu pores groupés, vraisemblablement chêne, polychromie.

Dimensions: hauteur: 122 cm, largeur: 35 cm, profondeur: 41 cm.

Saint-Jean-Baptiste est représenté en ascète portant une peau de mouton ou de chèvre laissant à nu les bras, une jambe et une partie du torse, conformément à la tradition occidentale. Il est en mouvement, tournant la tête et montrant l'agneau à ses pieds. Le saint a la bouche ouverte. Ainsi, le sculpteur l'a représenté disant: "Voici, l'agneau de Dieu qui ôte les péchés du monde", paroles avec lesquelles il salua Jésus.

### 5. Bibliographie:

R.L. Barclay, D.W. Grattan, A silicone rubber/microballoon mixture for gap filling in wooden objects, in *ICOM Committee for Conservation*, 8th triennial meeting, Sydney, 1987, vol. 1.

R. Barclay, C. Mathias, An epoxy/microballoon mixture for gap filling in wooden objects, in *Journal of the AIC*, spring 1989 vol. 28, n° 1.

D.W. Grattan, R.L. Barclay, A study of gap-fillers for wooden objects, in *Studies in Conversation*, n° 33 (1988).

Pamela Hatchfield, Note on a fill material for water sensitive objects, in *Journal of the AIC*, 1986, vol. 25, n° 2.

Nous sommes conscients que le bois de balsa est un bois très tendre, facilement attaqué par les micro-organismes. Mais les oscillations de HR étant importantes, il semble que le fissurage soit un danger au moins aussi grand que les attaques biologiques. Le balsa est aussi mécaniquement faible, ce qui le rend intéressant pour le comblage des fissures. Nous ne l'utilisons pas pour des restaurations structurales.

### 6. Saint-Antoine

Lieu de conservation: Chapelle de Locjean, Rosporden, Finistère, France. Auteur inconnu.

Date d'exécution inconnue: probablement XVIIème Siècle. Matériaux: bois de feuillu pores groupés, chêne, polychromie. Dimensions: hauteur: 148 cm, largeur: 50 cm, profondeur: 33 cm.



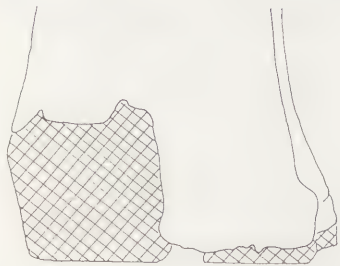


Fig. 15: Saint-Antoine. Base vue de dos, après restauration.

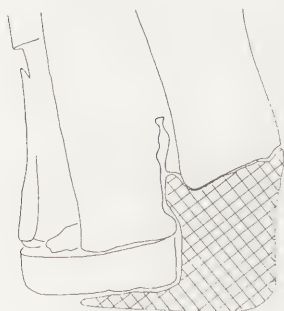


Fig. 16: Saint-Antoine. Base vue de côté, après restauration.

Saint-Antoine abbé (né vers 250 en Haute-Egypte) est à l'origine de l'ordre hospitalier des Antonites, fondé au XI<sup>ème</sup> Siècle. Le saint est représenté comme un vieil homme barbu, vêtu de la robe de bure de son ordre, avec capuchon, scapulaire et ceinture. Il tient dans la main gauche de livre de la règle des Antonites.

#### 7. Saint-Antoine

Le polyéthylène est plus perméable aux gaz (y compris la vapeur d'eau) que le polytéréphtalate d'éthylène. Ils sont tous deux imperméables à l'eau liquide. (Voir au sujet de ces matériaux: Jean Tetreault, Matériaux de construction, Matériaux de destruction, in "La conservation préventive", Actes du 3<sup>ème</sup> colloque international de l'ARAAFU, Paris, Unesco, 8-10 octobre 1992).

Mais l'expérience issue de la pratique de la conservation préventive (emballage pour le transport et les réserves) montre que les phénomènes de condensation sont plus souvent observés avec le polyéthylène. Est-ce dû à une différence d'épaisseur des matériaux utilisés et/ou à leurs réponses plus ou moins rapides aux changements de température?

Un autre interface possible serait une feuille de Gore-Tex (R) (ceci est une suggestion de Jon Braenne).

## Abrégé

Après l'histoire et la description du Christ, suivent l'étude approfondie du support et l'examen des polychromies successives. Les altérations graves provoquées notamment par un décapage récent sont expliquées. Le traitement consistant à atténuer les dégâts par une reprise du dégagement des surpeints et à redonner une lisibilité à l'oeuvre par une retouche réversible minimale est décrit. Dendrochronologie, analyses, documentation, complètent le travail. Publications et conférences dénonçant les dégâts irréversibles causés au patrimoine et notamment aux sculptures par incompétence, par manque de loi stricte protégeant les oeuvres et par manque d'organisation sérieuse et universelle d'un enseignement de la profession de "Conservateur-Restaurateur" devraient être réalisées en dehors des cercles spécialisés de l'IIC et de l'ICOM.

## Mots clefs

Sculpture polychrome, Christ en croix, XIV<sup>e</sup> siècle, retouche, dendrochronologie, cabachon, décor en relief



Fig. 1: Le Christ après traitement.  
(Copyright A.C.L.—Bruxelles.)

## La reprise d'une mauvaise restauration d'un Christ Mosan du XIV<sup>e</sup> siècle

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### Histoire

L'origine du Christ en croix, dit du Tombois, aujourd'hui conservé dans l'église de l'Institut Saint Berthuin de Malonne (Namur) n'est pas connue. Il pourrait provenir de l'ancienne abbatale. La tradition dit que le Christ aurait été dans la chapelle du Malpas, construite au XVI<sup>e</sup> siècle et détruite aujourd'hui. Il aurait ensuite été dans le cimetière de Malonne, dans un enclos situé au pied du clocher. Enfin, en 1868, on le déplace encore et cette fois pour orner l'entrée du nouveau cimetière situé sur la colline au lieu-dit Tombois. Il est alors en plein air sous un auvent.(1)

En 1984, un historien l'examine et décide de le confier à un prêtre qui le décape sans aucune opération de refixage des couches picturales. Son action est drastique et arrache presque la totalité de la couche picturale originale pour ne laisser paraître que la préparation blanche confondue avec la couleur originale, et beaucoup de lacunes nouvelles jusqu'au bois. En 1986, l'oeuvre est exposée dans la chapelle de l'Institut Saint-Berthuin. En 1989, le Christ entre à l'Institut Royal du Patrimoine Artistique pour étude et restauration (Fig.1).(2)

### Description

La sculpture de ce Christ en croix gothique en chêne polychromé (hauteur: 160 cm, largeur: 133 cm.) est particulièrement belle. Le Christ était suspendu par trois clous à une croix aujourd'hui perdue.(3) Son visage expressif et doux est penché vers l'avant, légèrement à droite. Ses yeux en amande semblent regarder le spectateur. Les pommettes sont saillantes. La bouche fine légèrement entrouverte laisse apparaître les dents.

La moustache rejoint une barbe assez courte, taillée en larges mèches et légèrement bifide. Son abondante chevelure est divisée par une raie médiane et maintenue par une couronne végétale tressée et plantée d'épines. Des mèches raides tombantes croisent curieusement les mèches ondulantes qui encadrent le visage, partent vers la nuque et s'y étalent en triangle.

Les bras tendus légèrement vers le haut forment avec le corps des lignes harmonieuses. La silhouette du corps est sinueuse et présente une double courbe. Sur le large torse, les pectoraux sont fortement marqués, ainsi que les côtes. Au centre du torse, une cavité ronde, sans doute prévue pour abriter une relique, devait être fermée par un précieux cristal de roche taillé. Elle est malheureusement vide aujourd'hui.

Le tissu du périzonium forme quatre plis en V sur la jambe gauche du Christ, moule les genoux et retombe des hanches en deux grandes chutes de plis aux multiples enroulements. Le vêtement est bordé d'un orfroi doré en relief parsemé de petits cabochons en verre coloré.

Les jambes croisées sont courtes. Cette sorte de déformation anatomique est très fréquente pour les Christs en croix qui étaient placés haut.

Les pieds sont posés l'un sur l'autre, le droit sur le gauche, les dix orteils apparents, formant la pointe d'un losange.

Le sang des cinq plaies est particulièrement abondant. Les gouttes qui jaillissent sont traitées en relief. De plus, le corps du Christ est couvert d'une centaine de petites blessures de flagellation représentées par une ligne noire d'où coulent de trois à quatre gouttes de sang également appliquées en relief.

Malgré cet aspect sanguinolant, ce n'est pas l'image de la souffrance, mais celle de la sérénité qui se dégage de cette oeuvre noble et élégante.



## Mise en oeuvre de la sculpture

### *Le support*

Le corps du Christ est taillé dans un tronc de chêne. La tête est sculptée dans la base du chêne, plus large, et les jambes dans la partie haute de l'arbre se divisant en branches. Après l'ébauche, on a procédé à l'évidement du dos. Ce travail a permis d'éliminer le coeur de l'arbre provoquant tensions, fentes de coeur et éclatement au séchage. Les blocs de chêne destinés à la sculpture des bras ont ensuite été placés, les tenons ajustés et chevillés au corps. Dans les creux des coups de gouge arrondis visibles dans le dos évidé, on a trouvé de la boue séchée. Nous l'avons interprétée comme un dépôt terreux dû à un trempage de la sculpture dans une eau d'étang ou de rivière après la taille et avant la polychromie, afin d'éliminer sucs et tanins.

Une autre observation concerne les pieds du Christ. Ils ont été brisés. Un bloc de bois faisant partie du tronc de base a été cassé et remplacé après quelques retailles du bois arraché, mais l'avant des pieds (depuis l'emplacement du clou) a été remplacé totalement par un bloc de chêne dont la coupe est orientée différemment. A la question de savoir si cet accident s'est passé au cours de la création de l'oeuvre ou postérieurement, il a été possible de répondre grâce à l'examen minutieux des polychromies qui toutes (originale et surpeints) recouvraient l'ensemble des pieds. L'accident s'est donc produit en cours de taille et a été réparé à l'aide d'un chevillage double (quatre chevilles) et de colle animale. Cette précision est très importante, car l'analyse dendrochronologique n'était réalisable que sur le fragment de chêne ajouté des pieds.

Après l'achèvement de la taille, on a fermé l'arrière à l'aide de deux plaques de chêne; l'une, encore visible, ferme la cavité à hauteur du périzonium, l'autre, disparue, fermait le dos.

Enfin, on a bouché à l'aide d'une cheville le trou d'étau situé au sommet du crâne du Christ, et on a fiché des épines en chêne dans la couronne.

### *Marouflage, préparation et polychromie*

Le bois a alors été encollé et localement couvert de toile de lin. Cette opération est appelée le marouflage: la toile recouvre les joints entre plusieurs pièces de bois, cache les noeuds afin qu'aucune fissure ou craquelure n'atteigne les couches picturales. On en découvre donc aux joints des bras, sous la plaie du thorax, sur les genoux et les jambes (noueuses), sur la réparation des pieds, et encore sur le dos, aux joints des deux planches de fermeture.

Une préparation blanche, composée de craie et de colle animale, a ensuite été appliquée sur l'ensemble de la pièce. Elle sert de base à la peinture mais surtout termine l'oeuvre formelle du sculpteur. En effet, et ceci est particulièrement à la mode au XIV<sup>ème</sup> siècle, elle permet de créer des décors en relief. Les bordures du périzonium sont ornées d'une série de petites perles réalisées dans la préparation et de verroteries bleues, vertes et rouges serties dans la préparation.

Les gouttes de sang sont réalisées dans la même matière. La préparation tiède est déposée en gouttelettes au pinceau sur plusieurs couches de préparation déjà poncées et réparées (retailées).

Le Christ est passé ensuite aux mains du doreur et du peintre. Les feuilles d'or découpées sont posées sur une mixtion ou mordant gras chargé ici de pigments ocrés. Les bordures du périzonium sont dorées, ainsi qu'un cercle autour du cristal de roche disparu.

La carnation est peinte d'un ton rose soutenu nuancé de gris bleuté appliqué de manière uniforme (peinture plate); ensuite le périzonium est peint en blanc sur la face et en gris perle au revers. Le blanc est parsemé de petites fleurs dorées à cinq pétales. La chevelure est noire, la couronne verte. Les détails tels que les yeux, la bouche, les plaies, sont achevés au pinceau fin. Le sang est réalisé en trois tons successifs: une ligne noire, une rouge vif, enfin un ombrage avec un glacis de garance.

### La vie de l'oeuvre et son état

Les statues de culte sont au cours du temps repeintes de nombreuses fois, soit remises au goût du jour, soit simplement rafraîchies. Il y a en général, malheureusement, une baisse de la qualité picturale et simultanément un empatement des formes. Ainsi, notre Christ a reçu six surpeints en six siècles, ce qui peut donner 18 couches picturales si on examine une goutte de sang! Ces couches successives ont manifestement protégé le bois des intempéries.

Les doigts de la main droite sont cassés et perdus, ainsi qu'un orteil et les épines de la couronne. Le cabochon central et de nombreux petits cabochons ont également disparus. Les fragments des pieds se sont disjointes.

Malheureusement au XX<sup>ème</sup> siècle, l'objet religieux a perdu son caractère sacré et trop souvent, sans rien connaître aux techniques polychromes d'antan, des personnes bien intentionnées se sont mises à gratter les oeuvres en bois ou en pierre polychromées. C'est ce qui arriva au Christ du Tombois qui se vit décapé jusqu'à la préparation blanche à l'exception d'une partie des gouttes de sang en relief qui avaient trop tendance à disparaître totalement.

### Traitement

Toute sculpture en bois polychromé continue à "travailler" lorsque l'humidité de l'air varie. Ainsi la polychromie a souvent tendance à se soulever, à se craqueler et enfin à se détacher du support.

Le premier travail sera de choisir un ou plusieurs fixatifs pour recoller les écailles branlantes de la polychromie. Ici, après plusieurs tests, c'est un acétate de polyvinyle dilué qui a été choisi. (colle Pattex blanche normale de Henkel diluée dans l'eau 50/50, mélange plus épais pour les reliefs et la toile: 60/40, et additionnée de quelques gouttes d'un agent mouillant Agepon de Agfa-Gevaert).

L'étape suivante consiste en un examen minutieux, sous microscope binoculaire, des différentes couches de polychromies. Nous l'appelons l'examen stratigraphique et topographique et le résultat de la recherche est inscrit en couleur dans un tableau. Cette étude est complétée par des prises d'échantillons étudiés en laboratoire (coupes).

Après l'étude les restaurateurs peuvent proposer un traitement. Souvent on se limitera à la conservation, car une restauration comportant l'enlèvement d'un ou de plusieurs surpeints nécessite un temps très long et un coût excessif.

Pour le Christ du Tombois, oeuvre particulièrement intéressante et même exceptionnelle dans le milieu mosan, il était indispensable de sauver les restes originaux situés sur toutes les plaies, dans les creux profonds du plissé du péri-zonium et dans la chevelure. Ce travail effectué avec un scalpel ophtalmologique sous microscope dura plus ou moins 480 heures. Le nettoyage des lacunes où apparaît le chêne fut aussi très long. Avant de recoller les fragments des pieds, l'étude dendrochronologique a été menée.

Enfin, quelques petits bouchages au niveau du support furent nécessaires et exécutés à l'aide de poudre de vieux chêne tamisé (150 microns) lié à la colle (acétate de polyvinyl dilué à l'eau 1/1). Ces rebouchages se situent aux joints des bras et aux zones de collages des fragments des pieds et des chevilles.

Quelques bouchages au niveau de la préparation ont été faits à l'aide de kaolin et de colle animale. Les lacunes rebouchées de cette manière ont été sélectionnées de la manière suivante: normalement on laisse le bois apparent et on l'éclaircit quand les lacunes se situent dans un ton clair. Or, à certains endroits les formes et la localisation des lacunes perturbent la lecture des plissés et des volumes. Ici, les remises à niveau à la préparation blanche se situent à la jonction des deux bras, sous la cavité du cabochon, et le long du sang de la plaie du torse. Il fallait ensuite envisager la retouche.

Il semblait impensable de retoucher ou plutôt repeindre l'ensemble de la préparation dans le ton original rose mauve des carnations. On obtiendrait une polychromie d'aspect néo-gothique lourde.

La retouche a alors été envisagée par étape. La chevelure presque intacte ne nécessitait que de petites zones de retouches: les zones blanches (préparation



originale visible) sont retouchées en noir (pigments secs liés au Paraloid B72 dilué dans l'alcool éthylique plus un peu de diacétone alcool) et les lacunes jusqu'au bois sont légèrement teintées, le bois restant apparent.

Le tissu du périzonium dont la couleur blanche originale peut visuellement se confondre avec la préparation n'a pas été retouché. Par contre, la bordure du périzonium, élément essentiel dans la définition des formes et dont plus des trois quart de la dorure était arrachée a été retouchée à l'aide de pigments ocrés liés au Paraloid B72 dilué dans l'alcool éthylique (additionné d'un peu de diacétone-alcool), sorte de glacis transparent donnant l'illusion d'un bord doré faisant revivre les quelques îlots d'or subsistants (Fig.2). Ensuite, le sang en relief peint



Fig. 2: Plissé du perizonium avant et après traitement. (Copyright A.C.L.—Bruxelles.)

d'un rouge très vif et dont de nombreuses gouttes étaient parsemées de lacunes blanches a été retouché par petites touches. Les plaies étaient de nouveau lisibles après l'intervention sur les rouges. Enfin, il fallait clôturer l'intervention de retouche par les carnations. Des îlots significatifs originaux subsistaient ça et là, mais ces surfaces étant si petites (un centimètre carré maximum) il était inadmissible de retoucher toute la surface. Après réflexion, le but de la retouche des carnations a été défini: le spectateur doit percevoir une différence de tonalité entre la chair du Christ et le tissu du périzonium.

La retouche a donc consisté à un minimum de petites touches picturales légères, juxtaposées, translucides et ne couvrant pas le réseau de craquelures. Le travail est discret, réversible et minimaliste. Pour protéger la retouche et la préparation encore visible, nous avons appliqué une très fine couche de cire micro-cristalline Cosmolloïd 80H très diluée dans le White-spirit. Malgré l'inadmissible intervention précédente le Christ a retrouvé beauté et dignité.

### La datation

#### *La dendrochronologie*

La dendrochronologie est une méthode scientifique de datation fondée sur l'observation des cernes annuels de croissance qui apparaissent à la section transversale des troncs d'arbre. Seule la pièce inférieure des pieds démontés permettait une analyse dendrochronologique. Sur ce fragment, sur une longueur de 10,7cm, on compte 133 cernes. C'est un chêne à croissance lente provenant probablement du bassin de la mer Baltique. L'absence d'aubier (bois jeune près de l'écorce) ne permet pas de déterminer la date exacte de l'abattage de l'arbre; de plus, vu la découpe des pieds, il manque probablement aussi un peu de bois de coeur (Fig.3).

Le cerne le plus jeune correspond à l'année 1307. Si l'on tient compte de l'aubier manquant (environ 17 ans en moyenne) on peut conclure que l'arbre n'a pas été abattu avant 1324, mais qu'il l'a sans doute été un peu plus tard, vu l'élimination par taille de bois de coeur.(4)



Fig. 3: Parties démontées des pieds; à gauche: zone d'examen dendrochronologique. (Copyright A.C.L.—Bruxelles.)

### *Style et comparaisons*

Cette oeuvre est de style gothique mosan. Cette école reçoit à la fois l'influence française pour l'élégance et le maniérisme, et l'apport germanique dans le goût du décor en relief des orfrois et de l'insertion de cabochons, enfin de l'expressionnisme du sang. Les Christs des Pietas rhénanes, d'expression très douloureuse, ont presque tous une polychromie comportant du sang en relief, de même que les Christs en croix de Bohême et de Pologne.(5)

Le Christ de Tombois est d'une facture proche de plusieurs Christs de la région étudiés par R.Didier (6), et il ressemble étonnamment à celui du Calvaire de Donceel daté entre 1330 et 1340. Il semble cependant être le seul Christ mosan en bois à avoir eu un cabochon "reliquaire" sur la poitrine,(7) le seul à présenter encore du sang en relief,(8) et un des seuls à conserver une bordure en relief à incrustation de verroteries.(9)

L'état très mauvais des Christs ou Calvaires comparables peut cependant laisser supposer que des décors polychromes du même type ont pu exister et être éliminés lors d'interventions anciennes ou récentes. On peut donc considérer cette sculpture comme un témoin exceptionnel de l'art mosan, réalisé entre 1330 et 1340.

### **Conclusion**

L'étude et la restauration du Christ de Tombois ont permis de mieux connaître l'aspect authentique des Christs mosans du deuxième quart du XIV<sup>e</sup> siècle.

Bien que la carnation originale ne soit plus perceptible que dans de très petits îlots, bien que le rythme donné par les couleurs alternées des plissés du périsonium ne soit plus lisible, et en dépit des nombreuses lacunes laissant apparaître le bois, la restauration a redonné à l'oeuvre solidité et harmonie.

La recherche pourrait être poursuivie par l'étude et la restauration du Calvaire de Donceel, abondamment surpeint, dont le sculpteur est probablement celui du Christ de Tombois.

Pour terminer, nous nous permettons d'exprimer un souhait: que les publications sur des restaurations de sculptures polychromes et l'information sur le métier spécifique de Conservateur-Restaurateur de sculptures se multiplient et se développent afin d'empêcher les trop fréquentes destructions de polychromies!

### **Notes**

1. F.G. Thiry, Bulletin du Cercle Archéologique de Malonne, n°5, déc. 1986, p.4. & notes manuscrites: A propos du Christ du Tombois.
2. Dossier I.R.P.A. n° 2L/47-89/4297. La restauration a été subsidiée par La Fondation Roi Baudouin et par la Loterie Nationale.
3. Pour l'histoire de la représentation du Christ: P. Thoby, Le Crucifix des origines au Concile de Trente. Etude iconographique, Nantes, 1959, p.44-45.
4. Analyse dendrochronologique réalisée par J. Vijnckier.
5. Plusieurs exemples dans le catalogue d'exposition: Die Parler und der Schöne Stil 1350-1400, t.1,2,3, Köln, 1978. & dans: W. Krönig, Reinische Vesperbilder aus Leder und ihr Umkreis, in Wallraf-Richartz Jahrbuch, XXIV, 1962, p.97-179.
6. R. Didier, Skulpturen des Maasgebiets aus des Jahren 1330-1360 vom Meister der Maria von La Gleize bis zu Gilles von Lüttich, in Westfalen - Hefte für Geschichte Kunst und Volkskunde, 55.Band, 1977, heft 1-2, Münster, p.8-29.
7. Cependant d'autres sculptures mosanes représentant, Vierges et Saints, conservent des cabochons (ou leurs traces): notamment: Saint Aubin de Bellevaux-Ligneuville, Saint Pierre et Saint Paul conservés au Landesmuseum de Münster, Vierge d'Annonciation mosane conservée au Victoria & Albert Museum de Londres etc.
8. Un autre Christ conservé à l'abbaye de Tongerlo présente du sang en relief dans la préparation, mais il est un peu plus tardif et considéré comme germanique. En effet, l'expressionnisme douloureux est proche du Christ de Breslau (publié dans 4. Die Parler...).
9. Un autre Christ mosan en bois polychrome provenant du cimetière de Bois-de-Breux (en dépôt au Musée d'art religieux et d'art mosan depuis 1983) possède le même type de bordure à cabochons sous de nombreux surpeints et est actuellement en restauration à l'Ecole des Arts Visuels de La Cambre, section Restauration d'Oeuvres d'Art.



# Working Group 6

Modern and Contemporary Art

Art moderne et contemporain





## Abstract

The exhibition "The Crisis of Abstraction in Canada: The 1950s" comprises 158 works of art, 125 of which are paintings. Many of the works are privately owned or belong to small institutions that do not have ready access to conservation facilities. The exceptional decision was made to treat the majority of the physically deteriorated paintings either at the National Gallery of Canada or on contract. Given the large numbers of works requiring treatment and the tight time constraints, it was decided to focus on structural soundness rather than appearance. A number of preventive and remedial care techniques were developed for the paintings requiring treatment. This discussion deals with the preventive care for the works on canvas. The non-intrusive methods of treatment opted for have proven to be extremely effective; these include the stretcher-inserts, stretcher-bar linings, rigid and padded backings.

## Keywords

Stretcher-inserts, rigid backing, padded backing, stretcher-bar lining, handling transit storage (HTS) frames, industrial and retail trade name paints, preventive conservation, canvas paintings, travelling exhibition

## Some Structural Solutions to the Question of Preventive Conservation Care for a Major Travelling Exhibition, "The Crisis of Abstraction in Canada: The 1950s"

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## Introduction

The making of art has always been exploratory; and exploration would seem to have become the very essence of modern and contemporary art. Although painters have been modifying their materials and methods since the profession began, most sources agree that the advent of commercially prepared materials brought about a profound change to the face of painting.

Research before, during, and after World War II produced many new industrial and retail trade name products such as the latex-based paints developed as a by-product of synthetic rubber. These were followed in the 1950s by such products as the aqueous acrylic dispersion wall paints<sup>(1)</sup>. Automotive finishes first produced in the 1920s<sup>(2)</sup>, were also utilized by certain artists during the 1940s and 1950s.

Some Canadian artists used the automotive finishes based on cellulose nitrate or alkyd resin for many of their paintings from the 1950s. The products, stove-pipe enamel and blackboard slating, were also utilized; although designed a) as protective coatings to be applied to rigid surfaces such as metal by spraying, dipping, or baking, and b) to last approximately ten years under harsh outdoor conditions. Artists applying such paints to canvas did not foresee the manner in which they would age and were disturbed at the way they did age. Also, the automotive paints were quite toxic for use by artists. As a result, the automotive finishes were not used extensively.

Due to the availability of such products, the fifties were a fertile period for the making of paintings; in many cases the industrial and trade paints were used along with artists' quality oils. Certain artists experimented with the addition of a solution of the acrylic resin Lucite 44 (R) to artists' oils allowing faster drying and gaining a certain luminosity. The late 1950s and early 1960s saw artists enthusiastically embracing the acrylic resin/solvent paint Magna (R) and the acrylic resin/water emulsion paints such as Liquitex (R).

Recently, this period became the focus for a large travelling exhibition mounted by the National Gallery of Canada (NGC). Given the use of such untraditional materials, and the fact that many of the works included in the exhibition were privately owned or from small institutions, it was felt that the condition of the works should be thoroughly understood prior to issuing an official request for loan. The author travelled to Western Canada and Southwestern Ontario to examine paintings. In the Montreal/Toronto areas, the examinations were contracted to private conservators. Of the 125 paintings in the exhibition, about 90 were identified as requiring some form of treatment; the majority of the works would come to the NGC for treatment. This initial examination was useful as:

- a) the physical condition of the paintings was made apparent to the owner before they were moved;
- b) all inscriptions were noted for the curator;
- c) colour photographs were taken, providing a useful check on the condition and identity of a work;
- d) accurate measurements of paintings/frames were taken by one person for catalogue entries and for estimates for materials for packing/crating; and
- e) any necessary treatments were identified.

Furthermore, because of the amount of work involved it was decided that treatment priority should be based on structural stability, rather than on purely

aesthetic grounds. For further details on the paintings from this exhibition, see the technical essay "Materials Used in Certain Canadian Abstract Paintings of the 1950s" published in the exhibition catalogue <sup>(3)</sup>.

As many of the works needed to be prepared prior to being photographed for the catalogue, the deadline for the treatments was the date when the catalogue material had to be submitted for publication, ie, several months in advance of the opening.

### Preventive Care Techniques

The author has relied on the general theories and writings of M.F. Mecklenburg, Assistant Director for Conservation Research, Conservation Analytical Laboratory, Smithsonian Institution, Washington, D.C., J.E. Gordon, Professor of Materials Technology, University of Reading, England, and Professor D. Westwood, School of Architecture, Carleton University, Ottawa, for the assessment and application of the following preventive care techniques.

The auxiliary supports for many of the paintings required replacement. For a number of paintings in this category, replacement was considered to be ill advised, given:

- a) the out-of-square format, which meant difficulty in accurately constructing replacements and therefore honouring the original intent to display the entire painting;
- b) the time and cost of replacement; and
- c) the new stresses and strains which would be induced into the original canvas.

The non-intrusive methods of treatment opted for have proven to be extremely effective; these include the stretcher-inserts, stretcher-bar linings, rigid and padded backings.

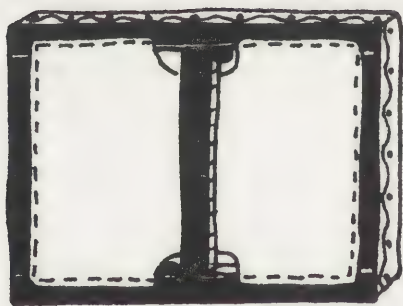


Figure 1

Stretcher-bar lining.

### Stretcher-bar Linings

Stretcher-bar linings were initiated at the Tate Gallery, London, in the early 1980s, as a quick way of preparing a painting for loan <sup>(4)</sup>. It has since been found through systematic research that the protection this technique gives is more than a quick fix <sup>(5)</sup>. At the NGC, the Restoration and Conservation Laboratory (RCL) has used stretcher-bar linings for several paintings in the exhibition (see fig. 1). Either a napped fabric such as linen or a multi-short fibred polyester was chosen a) for its "natural mechanical attraction" to the original linen or cotton canvas, b) it cushions movement initiated by vibration between the original and the lining fabric, and c) multi-short fibred fabric can also help dissipate shock waves transferred from the edge of the auxiliary support more readily than a monofilament fabric <sup>(6)</sup>.

A section of such a fabric was tacked temporarily to the original stretcher, measured and cut to size; it was then removed and U-shaped segments were cut out of the fabric at the points where the cross members were attached to the main body of the original stretcher. The cut edges of the stretcher-bar fabric were finished with the zigzag stitch on a sewing machine. The lining fabric was folded into flat pleats and slid between the cross members and the verso of the original canvas. The fabric was then pulled taut and attached to the outer edges of the original stretcher with staples inserted at short intervals. The tension should be tight, as this can help strengthen the rigidity of the entire structure, while affording excellent protection to the original canvas by minimizing contact with the cross members of the original stretcher.

### Rigid Backings

Backings were originally fitted for impact resistance, later their moisture barrier properties were recognised. It has also been found through empirical observation by conservators and through research <sup>(7)</sup> that the use of rigid backing boards attached to the verso of paintings can considerably diminish movement in the original canvas. The author in collaboration with the Canadian Conservation Institute <sup>(8)</sup> confirmed these earlier findings. The boards tested were Coroplast



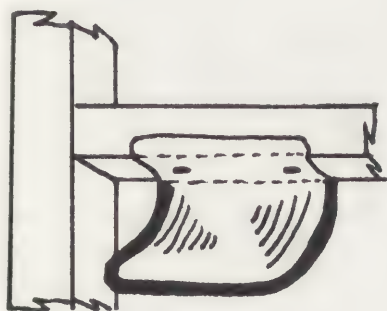


Figure 2

Hand hold.

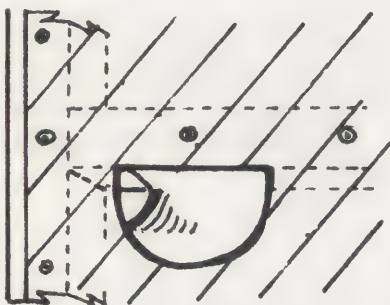


Figure 3

Hand hold

with backing board.

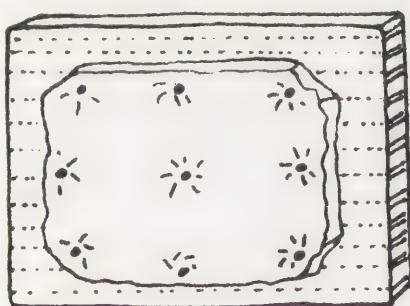


Figure 4

Padded backing.

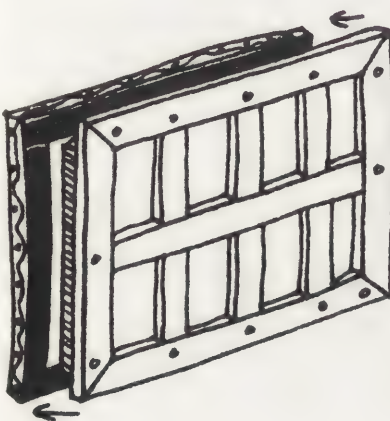


Figure 5

Stretcher-insert.

(R), untempered hardboard, and 0.5 cm thick aluminum honeycomb panel. Lightweight Coroplast (R) is excellent if well attached with screws (twenty centimetres apart) to the stretcher and cross members; hardboard adds weight and rigidity, and its effectiveness can also be enhanced by increasing the number of screws; 0.5 cm aluminum panel adds weight and extreme rigidity, but can only be used on a perfectly flat auxiliary support. The aluminum panel can be particularly useful if the original auxiliary support is especially inadequate and is difficult to replace. The author has used Coroplast (R) most consistently for this exhibition as it is lightweight, adaptable to the idiosyncrasies of an uneven stretcher, and can be made quite rigid in most cases. Coroplast (R) is made from a highly static material, attracting airborne dirt which can be deposited on the wall behind the work; this may pose a problem for private owners.

### Hand Hold

Paintings from the 1950s have minimal strip wooden frames, which means that attaching a protective backing board to large works can cause problems for handling. To avoid attaching bulky handles to the backs of the paintings, the author devised a simple handling system for works that have cross members.

A 0.2 cm thick aluminum sheet is cut into rectangle shapes of appropriate size and bent to form an L-shaped 10 × 10 cm guard, which is fastened with screws to the underside of the cross member (see fig. 2). The edges of the metal are covered with fabric, and when the guard is in place it is pulled forward at the bottom edge. The Coroplast (R) backing has a corresponding U shape cut out of it to allow a hand to grip the underside of the cross member (see fig. 3). In this way, access to the cross member is allowed, while protecting the verso of the painting from accidental blows. If transference of temperature and relative humidity is an issue, the area can be sealed by further shaping and gluing of the metal guard to the backing.

### Padded Backing

The purpose of this type of support is to minimize vibration/shock to the original canvas by absorbing vibration encountered in transit and diffusing any transfer of shock from the auxiliary support. A number of smaller paintings with loose canvases without cross members were supported with polyester batting. This padding was attached to the inside surface of the Coroplast (R), hardboard, or aluminum panel, using a double-sided pressure-sensitive adhesive. The polyester batting is stable, comes in a number of different sizes, and is approximately 2.0 cm deep. A paper pattern was cut to match the inside measurements of the stretcher. The material was then laid out and cut to the shape of the pattern. It is important that the padding material does not quite fill the space between the back of the canvas and the inside surface of the Coroplast (R) backing—a too thick insert of padding could cause pressure against the canvas verso and eventually cause damage to the ground and paint layers; too little padding does not provide sufficient support for these layers. The double-sided pressure-sensitive adhesive used is Ruban Scotch Brand Tape (R). The padding can also be attached mechanically to the backing by stitching with thread (see fig. 4). It is critical that the polyester batting is well secured to the backing board and cannot move. This method is most useful on “smaller” paintings (ie, 60 × 90 cm) but can also be successfully adapted to larger paintings with cross members. The batting is applied in two separate sections on either side of the cross member (a flap of batting can be inserted between cross member and canvas verso).

### Stretcher-insert

The original stretchers of many of the larger paintings were inadequate. The stress imposed by the pulled canvas caused distortion of the relatively slight wooden stretcher members; in many cases, both the horizontal and vertical stretcher members had bowed inward, imparting an hourglass appearance to all sides of the stretcher. To circumvent the logistics of fitting a new stretcher, an expandable wooden stretcher-insert was constructed—this fitted over, into, and screwed onto the original stretcher (see fig. 5). In the fitting process, the stretch-



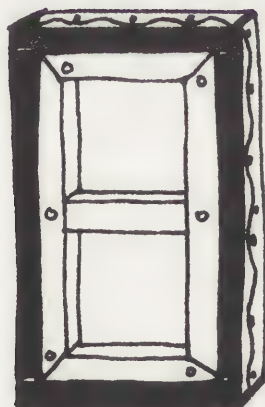


Figure 6

Strainer-insert.

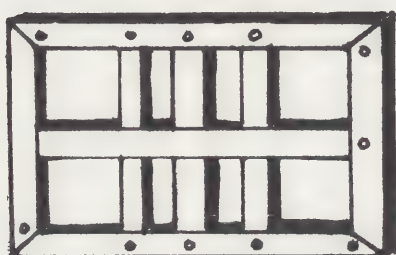


Figure 7

Stretcher for large  
heavy canvases.

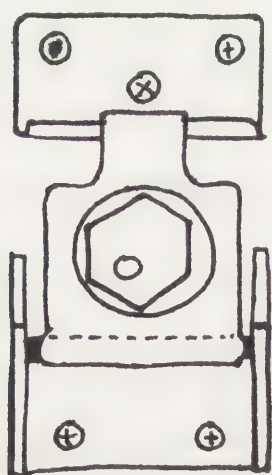


Figure 8

Simmons Link-Lock  
Fastener (R).

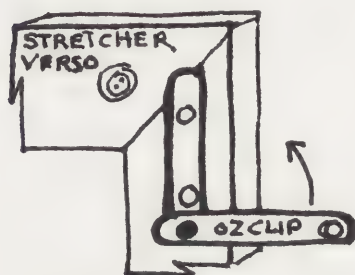


Figure 9

Ozclip (R).

er-insert could be expanded in order to press gently against the deep inside edge of the original stretcher members, taking up any slack in the original canvas. If the canvas required further support, fabric was attached to the inner side of the wooden insert (similar to a drylining, but attached to the stretcher-insert). This system has worked well on a number of the larger paintings. The entire structure became more rigid and the canvas no longer moved excessively when handled.

For medium sized paintings it was often possible to have a fixed wooden reinforcing insert constructed, which was then inserted flush with and screwed to the deep inside edge of the original strainer (see fig. 6). When it was considered necessary, fabric was attached to the inner side of the wooden insert. Again, the entire structure became more rigid and the canvas was stabilized.

### Large Stretchers

The author has found that if original stretchers of large heavy paintings are to be replaced, it is best to remount such paintings onto a specially designed stretcher<sup>(9)</sup>. If the painting has a long horizontal configuration, the supporting vertical cross members concentrate their strength at the centre of the horizontal outer members instead of being equidistant from one another (see fig. 7). In addition, the stretcher members should be sturdy.

### Handling Transit Storage (HTS) Frames

These wooden L section, handling, transit and storage frames were introduced at the Tate Gallery, London, in the 1960s and have been used increasing ever since. Such frames have been modified for specific in-house use at the NGC.

As cost, weight, and compactness were of importance, HTS frames, rather than crates, were used extensively for travelling most of the paintings in this show. The NGC HTS frames were constructed in three standard sizes—large, medium, and small—and were modified for this particular exhibition. Constructing the HTS frames in standard sizes allowed two similarly sized HTS frames to be placed face to face and joined with Link-Lock Fasteners (see fig. 8). The resulting unit of HTS frames was structurally more stable. Protective backings with a sealing layer of polyethylene film were attached at the verso and a sealing material was attached along the front edges of each frame. This ensured an enclosed air space for the paintings. The paintings were attached in the HTS frames with Ozclips (see fig. 9) instead of screws which can easily strip their wood channels after a few venues.

### Conclusion

The examination trip taken at the initial stages of the planning for this particular exhibition allowed for a greater understanding of the complexity of the issues facing NGC/RCL in the preparation of these complex and sometimes neglected works of art. This allowed for a more reflective, pro-active, and innovative approach to the treatment of the individual paintings. The use of the stretcher-insert, the active investigation of backing board types, and the understanding of the nature of the experimental materials used for these works were an important part of the preparation for the exhibition for a lengthy travel period.

### Notes

1. S. Hochheiser, *Rohm and Haas: History of a Chemical Company* (Philadelphia: University of Pennsylvania Press, 1986), 98.
2. R.B. Seymour and H.F. Mark, eds., *Organic Coatings: Their Origin and Development* (New York: Elsevier, 1990), 37.
3. M.H. Barclay, "Materials Used in Certain Abstract Paintings of the 1950s", in D. Leclerc, *The Crisis of Abstraction in Canada: The 1950s* (Ottawa: National Gallery of Canada, 1992), 205–231.
4. P. Booth, "Stretcher Design: Problems and Solutions," *The Conservator*, no. 13 (1989), 31–40.
5. T. Green, "Vibration Control: Paintings on Canvas Supports," and P.J. Marcon, "Shock, Vibration, and Protective Package Design," in *Art in Transit: Studies in the Transport of Paintings*, ed. M.F. Mecklenburg (Washington, D.C.: Ventura Publishers, 1991), 59–67 and 107–120.



6. If a painting sustains a blow when dropped while in the vertical position, shock waves can be transferred from the contact point, ie the floor, to the auxiliary support to the canvas.
7. T.Green, "Shock and Vibration-Test Results for Framed Paintings on Canvas Supports," in *Preprints of the 8th Triennial Meeting of the ICOM Committee for Conservation, Sydney, Australia 6-11 September 1987*, The Getty Conservation Institute (Los Angeles, 1987), 585-596.
8. P.J. Marcon, "Shock, Vibration, and Protective Package Design," in *Art in Transit: Studies in the Transport of Paintings*, ed. M.F. Mecklenburg (Washington, D.C.: Ventura Publishers, 1991), 107-120.
9. The original design for such a stretcher was first noticed by the author at a poster session at the 1987 or 1988 annual American Institute for Conservation (AIC) meeting; author not known.

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### Glossary

**Alkyd.** A generic name for coating resins based on polyesters, produced by the condensation of polyols such as glycerol or ethylene glycol, with polyacids such as phthalic anhydride and unsaturated vegetable oils; examples of alkyd-based paints used by artists are the retail trade automotive paints Cilux and Dulux.

**Batting or Wadding.** In present context, a soft pliable polyester material prepared in sheets or wide rolls and used primarily as an interlining in quilts.

**Blackboard Slating.** Shellac is frequently used as the binding medium, with pigments such as lamp or carbon black for colour; hardness and tooth are provided by materials such as quartz, calcite, rottenstone, and powdered pumice.

**Cellulose nitrate.** This product was manufactured by treating purified wood pulp or cotton linters with a nitric-sulphuric mixture, in either batch or continuous process. After thoroughly washing the product, it was reduced to the desired viscosity in a continuous digester at 150-170°C. It then had the water removed and "damped" with 30 percent ethanol, isopropanol, butanol, or toluene, and packaged in a 55-gallon open-headed drum; examples of cellulose nitrate-based automotive finishes used by artists are the retail trade name lacquers Cilco and Duco.

**Emulsion.** A stable dispersion of two immiscible liquids.

**Gilsonite.** The retail trade name for a natural asphalt generally found in Colorado and Utah. It is a lustrous black brittle mass and is soluble in alcohol. It can be the colouring agent in stovepipe enamel.

**Industrial Paint.** In the present context, these are products used in the manufacturing process, such as baked-on automobile enamels, which can only be bought with some difficulty by the general public.

**Retail Trade Name Paint.** In the present study, the term refers to paint products

such as interior and exterior wall paints, that are readily available to the general public.

Stretcher-bar linings. Also called camilinnings and stretcher linings.

Stovepipe Enamel. An oleo-resinous pigmented material containing linseed oil, Gilsonite, resin such as copal, turpentine, pigment such as carbon black, and possibly driers. It is used to protect metal stovepipes.

### Materials

Coroplast (R); corrugated polypropylene, 122 × 244 cm sheets: manufactured by Day, International (Canada) Limited, Cadillac Plastic Division. Distributed by: Canus Plastics Inc., Ottawa, Ontario, Canada, telephone (613) 232-2657.

Polyester batting (wadding) is available at most fabric stores retailing yard goods.

Double-coated Ruban Scotch Tape (R); pressure-sensitive tape no. 465 (5.0 cm wide): manufactured by 3M Canada Incorporated, London, Ontario, N6A 4T1; available at most office supply stores.

Link-Lock Fastener (R); manufactured by Simmons Fastener, Albany, New York, USA; high preloading—up to 230 kgs pull down pressure. Fingertip pressure on wing nut easily activates fastener. 180° turn lock or unlocks. Load-carrying capacity to 480 kgs tension. Wing nut can be eliminated and a bolt or screw head used for opening or closing (NGC uses this type). Canadian distributor: Kelly Leduc Ltd., Ottawa, Ontario; telephone (613) 778-3030; Fax (613) 778-0306.

Ozclips (R); manufactured by Panalpina World Transport, 200 Coward Street, Mascot, NSW 2020, Australia, telephone: 61 2 693-2600; available in two sizes, large (10 cm) and small (5 cm). Ozclip sets are supplied in a unit of four; type of clip used by the NGC is the large size without Rings. USA distributor: Moving Art, Box 11034, Alexandria, Virginia 22312, telephone (703) 941-8206.

Aluminum panels, 1. a) 0.6 cm aluminum core, and b) Fibrid (R) paper (phenolic coated) aramid paper core, both with aluminum skins; available in various sizes and depths. Manufactured by Railtech Limited, 325 Lee Avenue, Baie d'Urfe, Quebec, Canada H9X 3S3, telephone (514) 457-4760, Fax (514) 457-7111. 2. Alucobond (R), Manufactured by Consolidated Aluminum, St. Louis, Missouri 63141, USA: is a low density polyethylene core with aluminum skins; available in various sizes and depths.



## Abstract

This paper describes an examination of some of the materials and techniques used by Stanley Spencer for the series of paintings in Sandham Memorial Chapel, with reference to the causes of surface deterioration of the paintings. Analysis of the painting materials and samples of blanched material suggest that the blanching is caused by degradation of the oil binder in the paint and/or ground, by hydrolysis of esters to free fatty acids and associated loss of adhesion of inorganic particles within the paint layer. By a process of migration or simple abrasion of these inorganic materials, the varnish becomes separated from the paint layer and eventually breaks up, exacerbating desaturation and opacification which produces blanching. The mechanism of migration of organic and inorganic material through paint is yet to be examined.

## Keywords

Stanley Spencer, materials and techniques, blanching, fatty acids, oil paintings, scientific analysis

## A Technical Examination of Surface Deterioration of Stanley Spencer's Paintings at Sandham Memorial Chapel

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## Introduction

The paintings by Stanley Spencer at the Sandham Memorial Chapel at Burghclere have had a recurring history of surface deterioration (1). The term 'Blanching' has been used to describe the whitish appearance of the Stanley Spencer paintings in the Sandham Chapel (2). In some terminologies, 'blanching' describes a desaturation of a paint film, 'bloom' describes the opacification or whitening of a varnish, and 'efflorescence' describes the result of a migration of material to the surface (3). For brevity, this paper will refer to the appearance in the Spencer paintings as 'blanching.'

Stanley Spencer worked on the paintings at the Burghclere Chapel between 1927 and 1932. The scheme was conceived earlier while Spencer was on active duty during World War I, but it had taken almost ten years for him to find patrons, Mr and Mrs J L Behrend, who were willing not only to commission his work but also to build a chapel in which to house the paintings.

Spencer trained at the Slade under the tutelage of Henry Tonks and amongst contemporaries such as David Bomberg, Mark Gertler, Paul Nash and Edward Wadsworth (4). He specifically chose to study drawing rather than painting, a preference that directed his working practice throughout his life. He worked methodically, making detailed preparatory drawings which were then transferred to canvas by squaring up, the method employed at the Sandham chapel. Regarding his painting materials and technique, in 1955 Spencer himself professed that he 'never bothered about such things' (5). He also commented, 'It is noticeable that I am never preoccupied with *how* I paint. . .' (6). He almost always used the same suppliers, Bryce and Smith on Hampstead Road in London (7). A typical purchase included Winsor & Newton linseed oil paints and turpentine diluent.

## Condition and previous treatment

The works in the Sandham Chapel are painted on primed canvas. The upper register of paintings are adhered to the wall with interlayers of asbestos, boiled linseed oil, and gold size (8). The lower register of paintings are on wooden stretcher supports in niches. Most of the canvases were painted in the chapel itself, except for *Scrubbing Floors* and *Moving Kitbags* (the first two on the lower-left register), which were painted before Spencer moved to Burghclere, and *Making a Fire Belt* and *Washing Lockers* (the last two on the lower-right register), which were done after he had returned to Cookham.

The chapel was taken over by the National Trust in 1955, by which time the paintings had been treated twice for an uneven matt appearance, opacity, and 'bloom.' They were probably varnished for the first time during these treatments. Since then, the chapel has had three major restoration campaigns, and some of the lower register paintings have also been treated individually for the same problem. Reports describe various forms of 'blanching' resulting from poor saturation of the paint by the varnish, bloom in the varnish, whitening of the paint, broken varnish, and a crystalline deposit on the surface (9).

The chapel is currently in good condition with relatively stable environmental conditions. However, a building assessment report from 1955 suggests there were problems in the past, specifically a leaking roof, excessive moisture transfer from the walls, and condensation forming inside the chapel (10); improvements

\* Author to whom correspondence should be addressed.



were carried out. Since 1980, the paintings in the middle and lower registers on stretchers have had protective hardboard backings with holes drilled in them. They are not effective moisture barriers; therefore, the influence of moisture and pollutants on the blanching problem cannot be ruled out.

Other paintings by Stanley Spencer have been examined and similar surface defects found. Notably, about seven Spencer paintings at the Tate Gallery in London have been determined to exhibit some type of blanching, or have been suspected of it. These paintings include *Mending Cows*, *Cookham* (1915), *The Resurrection, Cookham* (1924–1926, just before Spencer started work on the Sandham Chapel), and *The Resurrection, Port Glasgow* (1947–195) (11, 12, 13). All of the following defects seem to relate to his technique: the use of very lean paint; the subsequent difficulty of saturating these layers with varnish; other medium rich paint layers sometimes applied over lean paint layers; not allowing one layer to completely dry before applying another; and the deterioration of these films with age.

### Methods of analysis

The present study aimed to characterise the forms of blanching found on the Sandham Chapel paintings and to consider other causes. Examination of the blanching included light microscopy of the surface of the paintings and paint cross-sections to identify the pigments and layer structure. Energy dispersive X-ray spectroscopy (EDX) and X-ray diffraction (XRD) were used to identify inorganic materials, such as pigments or ground. The scanning electron microscope (SEM) was used to characterise the surface of samples, in particular the blanching; Fourier-transform infra-red spectroscopy (FTIR) was used for examination of organic materials. Differential scanning calorimetry (DSC) provided information on organic and inorganic materials and their relative proportions. Further analysis of organic materials using time-of-flight secondary ion mass spectrometry (SIMS) and gas chromatography with mass spectrometry (GC-MS) is planned and the findings will be reported later, as will the results of environmental monitoring in the chapel.



Figure 1. *Tea in the Hospital Ward*, from the lower register of the Sandham Chapel, Burghclere. Painted by Stanley Spencer between 1927–1932.

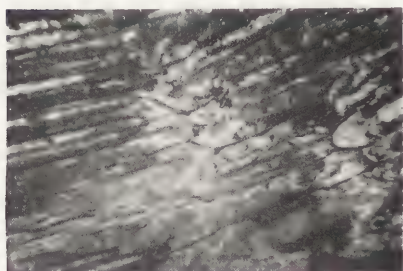


Figure 2. Micrograph from *Tea in the Hospital Ward*, showing the deposition of opaque white material on the painting surface and its relationship to the direction of the brushstrokes (magnification 11×).

### Examination of the paintings with regard to blanching

When the paintings were examined in August 1992, the patchy blanched appearance described in previous restorations was found to have recurred. The paintings in the top register that are on canvas adhered to the wall had deteriorated the most, particularly in the dark areas of paint where a white deposit, which could be easily dislodged with a scalpel, had formed on the surface. Similar deposits were seen on some paintings in the lower register including *Tea in the Hospital Ward*, which had other areas of paint with an opaque, desaturated appearance consistent with a poorly wetting varnish (See figs. 1, 2). At low magnification, the varnish appeared milky and cracked, in poor contact with the paint, with small opaque white particles of material on the paint surface.

The blanching did not immediately appear to have a common cause in all areas. For example, in one area of *Tea in the Hospital Ward*, the blanching followed a brushstroke while elsewhere in the same painting, spots of blanching appeared arbitrarily (See fig. 2). The blanching did not appear to be associated with specific pigments or colours.

### Materials and Techniques

Surface examination of Spencer's painting technique reveals that he had applied paint thinly with varying proportions of medium. A report on his techniques by Behrends on behalf of Spencer in 1959 described the use of linseed oil and turpentine in 1:3 proportions (14). Evaporation of the solvent has left a thin paint film through which the underdrawing on the white ground is clearly visible. In other areas, brushstrokes overlap or the paint is thicker and more saturated, presumably with more binding medium. The difference in thickness—and its relationship to blanching—is obvious when the painting is viewed in transmitted light; the blanching appears most dense in the thinnest areas of paint. It is present but less dense in the thicker areas.



Table I. Summary of analysis of inorganic materials.

Painting/sample	Ground	Paint	Blanching
<i>Camping at Karasuli</i> Blanched green hills. On primed canvas, adhered to the wall.  Blanched green-yellow foliage with encrusted deposit.	EDX: Pb and Zn in two layers, with more Pb in the top layer. (Under the canvas of all paintings adhered to the wall is a layer of asbestos and paint, Pb and Ba; and plaster Ca Sulphate and a lithopone paint layer, Al, Zn, Ba, Ca.	EDX: Complex mixed green, including red and yellow Fe (oxides); bone black Ca, P; Cu containing particles; a transparent yellow Pb (substrate for yellow lake).  EDX: Middle paint layer—Fe (oxides). UV light microscopy shows pink fluorescence on top red layer of paint, (red lake or zinc).	EDX: Zn (Mg, Cd).
<i>Ablutions</i> Brown opaque uniform with crystalline particles. Primed canvas on stretcher. Blue soldier's leg with white deposit.		EDX: Blue particles Si, Al, Na, S, Fe French ultramarine (with Prussian blue).	EDX: White material between paint and varnish Zn, (Fe, Mg).
<i>Riverbed at Todorovo</i> Unblanched green foliage. Primed canvas adhered to wall.	EDX: Zn and Pb in two layers, with more Pb in the upper layer.	EDX: Blue-black particles Zn, Pb (Fe, K, Cl) (White ground + Prussian blue); transparent red Pb, Zn, Ba (red lake + substrate); vermilion Hg, S; cadmium yellow Cd, K.	
<i>Map Reading</i> Unblanched green foliage. Primed canvas on stretcher.	EDX: Pb only, one layer (cross section may be incomplete).	EDX: Whole paint layer Pb, Cr, K, Fe, Si, S (viridian, Naples yellow, iron oxide red, red lake, lead white).	
<i>Tea in the Hospital Ward</i> Blanched bright blue jacket in foreground. Primed canvas on stretcher.  Unblanched dull blue jacket in foreground.	EDX: Pb and Zn in two layers with more Pb in the upper layer.  DSC: White Pb carbonate present. XRD: Cerussite, hydrocerussite, trace Ca silicates.	EDX: Blue paint S, Zn, Pb, Ca, K, Si, Al (Fe, Cu). French ultramarine, Prussian blue, lead white and zinc white.  EDX: Blue paint Pb, Zn, Fe, Ca, Si, Al (French ultramarine and Prussian blue).	EDX: Trace Fe, Mg, Al only (material mostly organic).  EDX: Pb (Mg, Al, Si, Fe, S). Pigment and dirt.
<i>Moving Kitbags</i> Samples of (a) ground and (b) blanching material. Primed canvas on stretcher.	EDX: Lower ground: Ca (Pb, Zn, Cl, Cu). Upper ground: Ca, Ba (Ti, K, S, Cl, Al). XRD: Calcite and trace ferrosilicates.		XRD: Ferrosilicate (as in the ground) in white blanching material.

Spencer's practice of using heavily diluted paint and of painting on top of layers that are not dry has produced craquelure patterns which are not always visible to the eye. In the brown paint from *Moving Kitbags*, one of the most blanched paintings in the chapel and one with a history of deterioration, a fine crazing is visible under low magnification in all the blanched areas. These fissures in the paint provide access for movement of materials from below and may be responsible for the extent of blanching in this painting.

The blanching is most visible in dark or saturated areas of colour, but examination using the light microscope on the surface of *Moving Kitbags* showed that some areas of light paint also had networks of fine craquelure and particles of loose material.

Table II. Summary of the analysis of organic materials.

Painting/sample	Ground	Paint	Blanching
<i>Camping at Karasuli</i> Blanched green hills.	FTIR: Mainly a drying oil.	FTIR: Aged drying oil.	FTIR: A polycyclohexanone varnish (AW2), wax; a natural glue. Brown sticky substance found in drips on surface (a gum).
<i>Tea in the Hospital Ward</i> Blanched and unblanched blue jacket foreground.	FTIR: A drying oil; saturated long chain free fatty acids, trace of resin, indication of ionic carboxylates or salts. Thermomicroscopy: Some material softens below 130°C, indicating resin (?). DSC: Suggested 40% binder.	FTIR: Drying oil.	FTIR: Saturated long chain free fatty acids (as in ground medium) from the white blanching material.
<i>Moving Kitbags</i> Analysis done on separate ground and blanching samples from brown paint.	FTIR: Drying oil, saturated long chain free fatty acids and long chain hydrocarbons (wax, from impregnation treatment). Possible trace glue; strarates; Calcium. DSC: 50% binder.		FTIR: Saturated long chain free fatty acids and a glue in white particulate material. Yellow-brown material; resin containing.

### Ground

Cross sections of the layer structure in a selection of the paintings from the Chapel suggested that Spencer used commercially-primed canvases with a double ground. The canvas was bought through the suppliers Bryce and Smith, whose stamp is on the reverse. The priming extends to the cut edges, evidence that the pieces were cut and stretched after priming and the ground layers were evenly applied in two layers. The lower ground is relatively thick and transparent.

EDX analysis of the ground layers from *Tea in the Hospital Ward* showed the presence of a mixture of lead and zinc in both layers, with a higher proportion of lead in the upper layer. This is consistent with commercial practice at the time, in which the more expensive and opaque lead white would have been used sparingly for the final opaque, thin ground layer. Analysis of a sample of the double ground by XRD gave powder patterns for both the hydrated and anhydrous forms of lead carbonate, cerussite, hydrocerussite, and calcium silicate. Surprisingly, no zinc compounds were identified, however, the sample was taken from the extreme upper edge. Due to the small sample size, it is possible that inhomogeneities in the ground materials could account for the absence of zinc in this analysis. (Table I summarises the inorganic analysis, Table II the organic analysis.)

Zinc and lead were also found (by EDX) in the ground from a painting, *Camping at Karasuli* from the uppermost register in the chapel. However, EDX analysis of the ground from *Moving Kitbags* identified a different double ground of chalk (lower layer) and chalk with barium sulphate (upper layer). An XRD powder pattern for the ground showed some lines for ferro-silicates with those for calcite. These materials were also commonly used for commercial primings in the 1920s and 30s. The visual appearance is virtually identical to the other canvases and bears the same Bryce and Smith stamp on the reverse.

Analysis of a sample from the ground from *Moving Kitbags* using FTIR suggested the presence of a drying oil, with a little glue, probably from the size layer (15). Figure 4 shows an FTIR spectrum of this sample of ground, showing carbonyl peaks at 1738 cm<sup>-1</sup> which are characteristic of esters in drying oils and waxes (See fig. 3). The peak at 1708 cm<sup>-1</sup> is characteristic of free carboxylic acids, in particular long chain saturated fatty acids (16). Twin bands at 720 and 730 cm<sup>-1</sup> are characteristic for long hydrocarbon chains, as observed in wax (17). The sample contained a low melting-point component, which softened at about 60°C,

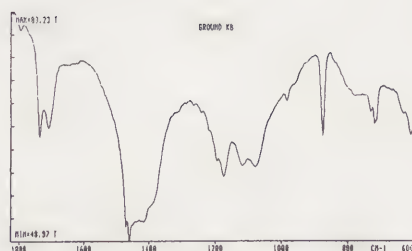


Figure 3. FTIR spectrum of a sample of the ground from *Moving Kitbags*.



indicative of the presence of wax and free fatty acids. Wax, observed on the reverse of the painting, was applied as part of an earlier conservation treatment (18).

DSC analysis of the ground from *Tea in the Hospital Ward* showed a two-peak exothermic curve that is typical for an oil-based medium; FTIR spectra showed the same absorption at  $1738\text{ cm}^{-1}$  as found in the ground from *Moving Kitbags* (19). Further peaks at  $1621$  and  $1534\text{ cm}^{-1}$  suggest that ionised carboxyl groups are present (metal soaps) (20).

FTIR also confirmed the difference (previously analyzed using EDX) in the inorganic components of the grounds from the two paintings. DSC measurements suggested that the ground from both paintings contained a higher than average proportion of medium: 40% for *Tea* and 50% for *Moving Kitbags*, measured as weight loss after oxidative degradation of organic components.

The acid value of the grounds from *Moving Kitbags* and *Tea in the Hospital Ward* was found to be 50 and 34 respectively; the result from *Moving Kitbags* may be affected by the wax in the ground. The values are comparable to acid values for aged dammar (21).

#### Paint layers

The paint was applied thinly, in one to three layers, with an average thickness of 20 microns. Spencer most often uses complex pigment mixtures, for example, the green foliage in *Map Reading* is a mixture of viridian, Naples yellow, iron oxide reds, red lake, and some lead white, as determined by EDX. Other pigments identified (using EDX) in the paintings include vermilion, red iron oxide pigments, yellow ochre, cadmium yellow, yellow lake, and two different red lake pigments. A cross-section from *Ablutions* contained lake particles that showed a characteristic pink fluorescence in ultraviolet light. Small dark blue particles of synthetic ultramarine have been used in several paint mixtures, including the boys' blue jackets in *Tea in the Hospital Ward*.

Analysis of the binding medium of the paint layers from *Camping at Karasuli*, *Moving Kitbags*, and *Tea in the Hospital Ward* suggests a drying oil was used.

#### Varnish

All the paintings are varnished with one or more layers which are clearly visible in cross section and SEM (See fig. 4). Fragments of paint and varnish from blanching areas showed the varnish layers to be disturbed and discontinuous, with particles of opaque white material apparent in cracks in the paint and varnish, in the varnish itself (a synthetic resin), and on the surface.

#### Blanching

SEM was used to examine the surface of samples of blanching and non-blanching paint to observe the surface characteristics of the material in detail and the relationship between all the layers. Electron micrographs showed the paint film generally to be extremely lean, with very little medium visible in some samples. A sample from the blanching brown paint on *Ablutions* shows a typically blanching area (See fig. 5). Inorganic particles with a hexagonal shape similar to particles of lead white are visible on the paint surface. Adjacent to these inorganic particles are fragments of broken varnish and other organic material. The fractured varnish is clearly visible under low magnification; in the SEM, it can be seen as light grey flakes on the paint surface (See fig. 5). Both inorganic particulate material and smaller less regularly shaped organic material are visible in cracks and on the surface of the varnish. Figure 5 shows the material deposited in such quantity that a discrete layer has formed on the surface of the varnish. This layer is relatively rough and about 1–2 microns thick.

Samples of the deposit were removed from the surface of the blanching areas of the paintings for analysis. Lead and zinc were identified by EDX in the blanching on dark brown paint in *Ablutions* and on the dark green paint on *Camping at Karasuli*. Lead was found in the blanching material from the blue jacket in *Tea*

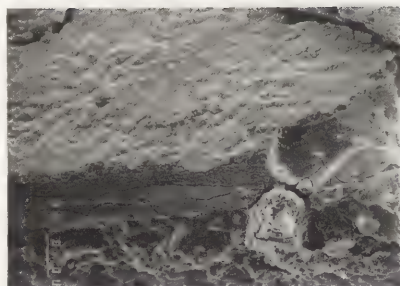


Figure 4. SEM micrograph of blanching green paint in *Camping at Karasuli*, showing the layer structure of the painting: lean paint, varnish layers with deposits of opaque white material in cracks and on the surface (magnification  $1220\times$ ).

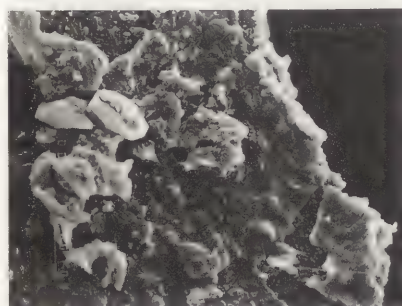


Figure 5. SEM micrograph of blanching brown paint from *Ablutions*, showing a lean paint film, broken varnish, other organic material, and inorganic particles showing hexagonal platelet structure characteristic of lead white (magnification  $1520\times$ ).



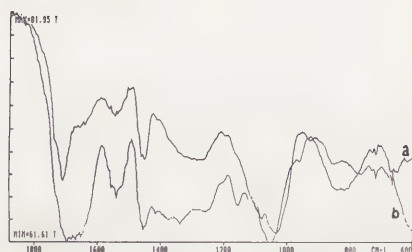


Figure 6. FTIR spectra of the blached material from *Moving Kitbags*. The sample contained white particulate material (a) and transparent yellow-brown material (b).

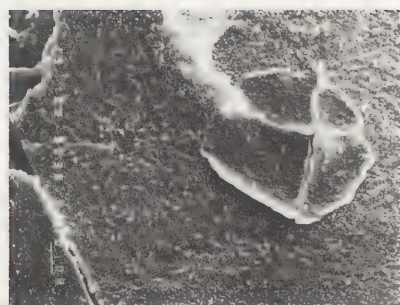


Figure 7. SEM micrograph showing varnish fracture caused by movement of loose material beneath. Sample from *Riverbed at Todorovo* (magnification 1020 $\times$ ).

in the *Hospital Ward*. The sample of blanching from the surface of the brown paint in *Moving Kitbags* contained the elements S, Mg, Al, and Si. The elements present in samples of blached material were, in general, consistent with elements in the paint and ground layers, suggesting that loose pigment particles were present in the blached material on the surface or that sampling removed pigment.

Samples of blached material were taken from *Tea in the Hospital Ward* and *Moving Kitbags* for organic analysis. The FTIR spectrum showed a peak for long chain saturated fatty acids at  $1708\text{ cm}^{-1}$  and the twin bands at  $720$  and  $730\text{ cm}^{-1}$  in both samples (See fig. 6). A shoulder peak at  $1740\text{ cm}^{-1}$  in the spectra from the white portion of the sample from *Moving Kitbags* suggested the presence of esters; this will have to be confirmed by GC-MS or another suitable separation technique at a later date (See fig. 6a). Samples from both paintings contained brownish fragments; the analysis of this portion from *Moving Kitbags* shows absorption characteristics suggestive of a natural resin or glue (See fig. 6b).

DSC analysis of the blached material from *Tea in the Hospital Ward* showed a two-peak exothermic curve, which is similar to degradation of long chain fatty acids. A peak at  $500^{\circ}\text{C}$  indicated the presence of a synthetic resin (22).

### Discussion

The cause of blanching in the paintings in this study may be directly related to the artist's materials and techniques. Three components were identified in loose surface material from blached paintings; varnish, fatty acids, and inorganic pigment. Although the techniques of analysis of organic materials using FTIR has not provided precise or detailed characterisation of materials, results suggest the presence of some materials for which there is corroborative documentary evidence.

First, several previous restorations have included varnishing and subsequently, cleaning and revarnishing. Broken fragments of varnish contribute greatly to the blached appearance of the paintings. The deterioration process which leads to blanching includes progressive loss of contact between the paint and varnish; the varnish breaks up, causing increased light scatter at the surface.

Long chain fatty acids identified in blanching on the surface and grounds of two paintings are probably degradation products of esters in the oil binding medium. The relatively medium rich ground layers are more likely to yield significant degradation products.

The third component of the blanching material is inorganic, containing elements also found in the ground and paint layers. This suggests that pigment particles are present on the surface with the blanching material.

One hypothesis which could account for these findings is that pigment particles from the leanly bound paint film and possibly from the ground become loose as the binder degrades. The degradation products from the binder and loose pigment particles cause desaturation of the varnish. The separation of paint and varnish proceeds as the degradation and migration in the layers beneath continue; material comes to the surface at first by accessible routes such as cracks in paint and varnish, until finally the varnish layer fragments (See fig. 7).

This hypothesis demands further examination of why the materials, specifically the binding medium, in these paintings degrade at such a rate to produce blanching. Hydrolysis of esters and the production of free fatty acids occurs in the presence of moisture, most rapidly in acid or alkaline environments. The grounds of the paintings contain alkaline pigments. Other additives (such as surfactants) present in the commercially primed grounds may influence the chemical environment; the formation of soaps may also play a role.

The blanching of the Spencer paintings may be linked with the manufacturing methods for oil paints and primings in the 1920s and 1930s. This has a bearing on other 20th century paintings that have blanching problems. The early 1920s were a time of experimentation by paint manufacturers and other materials may have been added during manufacture.



Further analysis of paint, ground, and blanched material using GC-MS to confirm the presence of organic components may provide further evidence for the accelerated hydrolysis of the oil binder. Comparative analyses of contemporary paint samples is also planned.

There is no clear evidence to explain how materials such as fatty acids migrate to the surface. Koller has proposed that the saturated fatty acids migrate to the surface with the liquid unsaturated fatty acids which are then oxidised at the surface, while the saturated fatty acids remain as a loose crystalline bloom (23). This explanation does not, however, address the process by which the fatty acids move through the layers in the painting.

Environmental fluctuations may contribute to blanching; the importance of such changes will be assessed when environmental monitoring is complete. It is suggested, however, that any moisture held in the plaster walls that penetrates the canvases does not cause blanching, but does exacerbate the movement of the material through the paint film. The recurring cycle of blanching in these paintings means the paint film continues to be disrupted as material migrates through it; voids and fissures form, increasing the ease of passage for further degraded material to migrate.

### Conclusions

From these studies of the Stanley Spencer paintings in the Sandham Chapel, the observed blanching is thought to be caused by degradation of the oil binding medium in the paint and ground. Degradation of esters in the oil film and production of fatty acids may be accelerated by alkaline hydrolysis; the inclusion of alkaline inorganic pigments in the ground may provide an alkaline environment. As degradation of the binder proceeds, inorganic pigment may be released and separation of paint and varnish occur. Fragmentation of varnish, the presence of inorganic pigment, and free fatty acids produce a blanched appearance by scattering light.

Explanation of the physical process by which degradation products move through the paint layers to the surface is not clear. The cause of accelerated degradation of the binder is the subject of further study; detailed characterisation of the binder using GC-MS, and comparison with contemporary paint samples may elucidate these processes.

### Acknowledgements

Special thanks is offered to Christina Sitwell, National Trust, who organised the project; Dr. Jennie Pilc, National Gallery, London, who examined a sample from *Camping at Karasuli* using FTIR; The Tate Gallery Conservation Department, for allowing us access to the conservation records of Stanley Spencer's paintings; the Department of Physics, Kings College, London University, and Link Analytical, UK Ltd., for the use of the JEOL T100 Scanning Electron Microscope with a LINK AN10 analyser; and Bill Luckhurst, for his help.

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## Abstract

Winsor & Newton artists' oil colours were aged thermally, photochemically and by combinations of the two. Thermal ageing induced dramatic deterioration of paints containing lead white while having little effect on Titanium white-containing samples. Lead white paints prepared with safflower oil yellowed to a level comparable to those prepared with linseed oil. Oil paint films were examined in cross-section with the ultraviolet fluorescence microscope. Interesting comparisons were made between samples that had deteriorated differently. The hue and intensity of a sample's autofluorescence seemed particularly sensitive to differing ageing environments. The response of paint films to the fluorochrome Rhodamine B indicated more generally the level of deterioration, and corresponded roughly with property changes detected at a macroscopic level. The performance of Rhodamine B showed that paint films did not deteriorate uniformly throughout their thickness. The response of samples to Rhodamine B and certain physical properties indicated that accelerating deterioration generated surface characteristics which were not representative of paint films maintained under ambient conditions, but that the material equilibrated within months of ambient storage.

## Keywords

Accelerated deterioration, artificial ageing, microscopy, ultraviolet fluorescence, Rhodamine B, oil paint, staining

## Accelerated Deterioration of Artists' Oil Paints: An Assessment Involving Ultraviolet Fluorescence Microscopy

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## Introduction

Research undertaken at the Tate Gallery in 1991–92 involved the preparation of reference paint films which were subjected to accelerated deterioration. The condition of the paint films was critical to their intended application (1). This paper compares paint films deteriorated by exposure to elevated temperature, to intense illumination and to two combinations of the two. Both macroscopic and microscopic properties were observed to indicate whether the composition of paint films or the deterioration environment was dominant in determining the condition of the reference materials and their response to the fluorochrome Rhodamine B.

## Sample range

Paint films were prepared to represent pigment types with a range of oil absorbencies, and which contribute to the drying of oil media to varying degrees. The hue and autofluorescence with ultraviolet excitation was also taken into consideration, given the intended application of ultraviolet fluorescence microscopy and staining with Rhodamine B which fluoresces in the red-orange range.

Paint films were prepared using Winsor & Newton artists' oil colours. Table 1 details the sample range.

Films of approximately 70  $\mu\text{m}$  thickness were applied to Melinex (4). In addition, samples (ii), (iv) and (vii) were applied to Melinex which had been primed with Foundation White; this was intended to provide information about medium migration between layers as well as indicate what drying behaviour may be imparted to a paint film by the presence of lead in an adjacent layer.

## Method: accelerated deterioration programs

Films of Foundation white were exposed to a temperature of 60°C at 52% RH for 40 hours to accelerate drying prior to the application of paint layers. The deterioration environments comprised thermal deterioration, photochemical deterioration, thermal deterioration followed by photochemical deterioration, and photochemical deterioration followed by thermal deterioration.

Thermal deterioration was carried out at 70°C and 50% relative humidity, with negligible light. The temperature was selected at the lowest level by which it was estimated significant deterioration would occur within two months. Conditions were achieved in a Fisons BR185H.WCC climate-controlled oven. Within the oven, samples were enclosed in a Perspex box, distributed on Perspex shelves lined with acid free blotting card; this unit buffered samples against any fluctuations in levels of environmental control. Open trays of activated carbon were included on each shelf within the unit, to absorb gases evolved in the process of deterioration and any emissions from materials within which the paint samples were enclosed.

For the photochemical deterioration, samples were distributed on a reflecting aluminium surface in polyethylene trays and positioned on the roof of the Tate Gallery. Trays were installed to face South at a 45° angle to horizontal to receive direct sunlight during summer. The light was filtered through the glass top and an inner sheet of UVA Perspex (R) to exclude ultraviolet radiation and simulate museum lighting. Draught excluder was applied beneath the glass tray fronts. Sheets of acid free blotting card and sachets of activated carbon were incorporated

Table 1. Winsor &amp; Newton artists' oil colours sample range.

	Paint type	Pigment composition <sup>2</sup>	Oil medium
(i)	Cremnitz white	lead carbonate	safflower
(ii)	Yellow ochre	(cerussite & hydrocerrusite)	
(iii)	Ivory black/Cremnitz white (1:6 by volume)	iron oxide magnesium aluminium silicate	linseed
(iv)	Ivory black/Titanium white (3:4 by volume)	calcium phosphate/ /titanium dioxide, magnesium aluminium silicate	linseed
(v)	French ultramarine/Cremnitz white (1:2 by volume)	sodium aluminium silicate, magnesium aluminium silicate/	safflower
(vi)	French ultramarine/Titanium white (3:2 by volume)		linseed and safflower
(vii)	Cobalt blue/Titanium white (3:2 by volume)	cobalt-aluminium oxide <sup>3</sup> /	linseed
(viii)	Foundation white	lead carbonate and zinc oxide	linseed

to buffer relative humidity and absorb gaseous emissions. ISO Blue Wool Standards 1–8 were exposed under the same conditions.

The other two environments (thermal deterioration followed by photochemical deterioration, and photochemical deterioration followed by thermal deterioration) were included to offset the imbalance in deterioration mechanisms likely to occur in the thermal and photochemical deterioration environments, though it is not certain whether deterioration induced by consecutive exposure to heat and light sources bears any similarity to that induced by simultaneous exposure or diurnal cycling at reduced levels.

Paint films were sampled at various stages. Table 2 details the exposure history of each sample range.

### Results

The deterioration of a paint film is dependent on its composition, condition, and the environment to which it is exposed. Property changes will reflect oil-pigment interactions and pigment-pigment interactions.

Macroscopic and chemical differences between materials deteriorated by different mechanisms have periodically been investigated, and Feller has long discussed options for accelerating deterioration (5, 6). Paint films in this study exhibited predictable differences according to the method of ageing and pigment composition. However, it was interesting to observe what properties were reversible when a sample was transferred between thermal and photochemical deterioration programs. Subsequent microscopic examination of paint cross sections revealed further information about the response of materials throughout a layer rather than simply at a surface level. It was apparent that paint films exposed to elevated temperature had reached a significantly more advanced state of deterioration than light aged ones. This has to be considered in any comparison of samples aged by the different methods.

Both macroscopic (colour changes, weight changes, initial drying, dimensional changes, and brittleness) and microscopic (autofluorescence, volumetric changes, and response to Rhodamine B) observations will be discussed.

### Colour changes

The colour of samples in CIELAB units was measured initially once paint films were surface dry and then at progressive sampling stages throughout the deterioration programs.

Thermally deteriorated samples generally showed the greatest colour change due to yellowing of the oil medium, although pigment type played an important role in the degree to which yellowing occurred. Paints mixed with Cremnitz



Table 2. Exposure environment, paint films and samples.

Exposure program	Exposure history	% Weight loss (Cremnitz White)
Controls		
Unprimed	light ambient studio environment from preparation	
Primed	Foundation White i) 18 days in light ambient studio environment from preparation	
	ii) 40 hours continuous exposure at 60°C, 50% RH	
	iii) 1 day in light ambient studio environment prior to paint application	
	iv) light ambient studio environment from paint application	
Thermal deterioration	<ul style="list-style-type: none"> <li>initially as for Controls</li> <li>light ambient studio environment 28–31 days (unprimed), and minimum 10 days (primed)</li> <li>sample range T1: 7 days (162 hours) at 70°C, 50% RH (6.8.91–13.8.91)</li> <li>sample range T2: 15 days (370 hours) at 70°C, 50% RH (6.8.91–22.8.91)</li> <li>sample range T3: 35 days (847 hours) at 70°C, 50% RH (6.8.91–16.9.91)</li> <li>sample range T4: 50 days (1231 hours) at 70°C, 50% RH (16.8.91–30.10.91)</li> </ul>	   2.46 3.69 4.51 5.33
Photo deterioration	<ul style="list-style-type: none"> <li>initially as for Controls and Thermal range prior to thermal exposure</li> <li>sample range P1: 29 days roof exposure (22.7.91–21.8.91) fading to Blue Wool Standard Cloth #3–4</li> <li>sample range P2: 65 days roof exposure (22.7.91–26.9.91) fading to Blue Wool Standard Cloth #5</li> <li>sample range P3: 101 days roof exposure (22.7.91–30.10.91) fading to Blue Wool Standard Cloth #5–6</li> </ul>	  1.81 2.27 2.27
Thermal/photo deterioration sequence	<ul style="list-style-type: none"> <li>initially as for sample range T2</li> <li>sample range TP: 40 days roof exposure (23.8.91–3.10.91)</li> </ul>	5.22
Photo/thermal deterioration sequence	<ul style="list-style-type: none"> <li>initially as for sample range P2</li> <li>light ambient studio environment (26.9.91–18.10.91)</li> <li>sample range PT1: 13 hours at 70°C, 50% RH (18.10.91–21.10.91)</li> <li>sample range PT2: 37 hours at 70°C, 50% RH (18.10.91–25.10.91)</li> </ul>	2.81 4.02

white changed hue more significantly than the same paints mixed with Titanium white. Foundation white and Cremnitz white are both lead based paints (although the former contains a proportion of zinc white), but are prepared in different drying oils, linseed and safflower respectively; the extremes of yellowing were slightly greater with the linseed oil, but after subsequent exposure to light ambient conditions and with photochemical deterioration, the hue of the two films became very similar. Where the lead white was present in an adjacent layer rather than in the film, the increased colour difference compared to the same paint film unprimed occurred specifically in the initial stages of deterioration and may primarily reflect migration of oil medium from the paint layer to the priming.

Thermal deterioration initiated a further level of discolouration in samples of French ultramarine mixed with Cremnitz white, resulting in loss of hue and darkening of the paint film presumably due to hydrogen sulfide emission from the ultramarine pigment and resultant formation of lead sulfide. Transfer of these samples to a light environment reversed the yellowing of oil media, but darkening of the paint film did not revert. This phenomenon has been associated with the use of impure ultramarine which contains free sulfur, but it is yet to be seen whether the same discolouration will occur in paint films not exposed to elevated temperature (7).

Oil media were generally bleached by exposure to light, evident particularly in white samples. However, there was little to distinguish between paint films exposed to intense and ambient light levels over the duration of the program or those transferred to a light environment after an initial period of thermal deterioration. Paint samples initially exposed to light and then exposed to an elevated temperature were observed to yellow significantly within hours, but this colour shift was generally reversed after samples were returned to a light environment. Continued exposure to light ambient studio conditions promoted fairly consistent trends of colour change in samples at a surface level irrespective of the preceding deterioration environment. However, yellowing of oil media was also observed where oil from a paint layer had penetrated the priming layer beneath it. The region of penetration was evident on the underside of the priming, visible through the Melinex substrate. Samples initially exposed to elevated temperatures exhibited a more intense yellowing than those subjected to photochemical deterioration; subsequent thermal or photochemical deterioration did not significantly reverse these states, even though surface characteristics were altered.

### **Weight changes**

Weight changes were monitored only in samples of Cremnitz white. Measurements were concerned with weight loss incurred during deterioration rather than immediate changes that might be observed with oxygen uptake on drying. Weight loss (expressed as a percentage of total film weight prior to accelerated deterioration) indicated the relative extent of change experienced by the paint media of samples exposed to different deterioration environments (Table 2).

### **Initial drying**

The rates at which paint films "dried" were not systematically monitored. However, general observations were made regarding relative film properties during the initial stages of drying and at points throughout the programs of accelerated deterioration.

Relative initial drying rates did not correspond to those anticipated given the natural interactions between pigments and media used in this study. This suggests that added driers dominated the first stages of drying, so that paint films containing Titanium white were observed to firm more rapidly than those containing lead white. Pigment composition appeared to have more direct influence over film properties at more advanced stages of deterioration.

### **Dimensional changes**

Film thickness has not been monitored. Changes in surface area have been inferred simply from crack formation or obvious changes in the perimeter boundaries of paint films. Dimensional changes were only noticed in primed samples. Contraction took the form of parallel cracks in the direction along which paint films had been drawn out. The paint films also contracted in from the perimeter of the priming layer.

Contraction was evident in all samples of primed Yellow ochre, including control samples, regardless of deterioration environment. Primed samples of Cobalt blue/Titanium white contracted after any exposure to elevated temperature, while Ivory black/Titanium white exhibited only minor cracking in samples initially deteriorated thermally.

### **Brittleness**

Brittleness of paint films was monitored by a process of hole punching; observations were made regarding the characteristics of the punched disc and the extent to which sampling promoted brittle fracture in adjacent paint.

Thermal deterioration caused lead-containing samples to embrittle rapidly; Titanium-containing samples retained significantly more cohesion when exposed to the same conditions. Photochemical deterioration did not induce such dramatic embrittlement, in fact samples prepared with Cremnitz white remained



almost soft after ageing. However, the brittleness of primed samples of paints mixed with Titanium white was greater with exposure to intense light in comparison to unprimed films of the same paints, particularly primed Ivory black/Titanium white and primed Cobalt blue/Titanium white, while primed Yellow ochre was relatively unaffected.

### Autofluorescence

Autofluorescence of paint samples was observed using a Carl Zeiss Jenamed 2 ultraviolet fluorescence microscope. Cross sections were photographed using Kodak 200 ASA Daylight colour reversal film and characteristics were noted during the examination of individual samples and by comparing photographic images.

Autofluorescence arises from sample composition and deterioration environment. Deterioration generally increased the intensity of autofluorescence; thermal deterioration induced more significant fluorescence than photochemical deterioration. In the latter case, some samples exposed to intense illumination initially underwent a reduction in autofluorescence at the surface of the paint film before continued exposure resulted in a gradual increase in intensity through the bulk of the medium.

The autofluorescence of thermally deteriorated paint films was also quite different in hue from samples exposed to alternative deterioration environments, tending towards yellow rather than white. Samples transferred between photochemical and thermal deterioration programs generally experienced associated shifts in autofluorescence, though macroscopic colour changes occurring with second stage thermal deterioration were not always reflected in autofluorescence. French ultramarine/Cremnitz white was a notable example.

A significant number of samples exhibited fluorescence properties at their perimeter which differed from the rest of the layer. Bands of reduced fluorescence were common at the upper surface of paint layers, particularly those photochemically deteriorated, sometimes with a less distinct band along the lower surface. However, there was not always an obvious correspondence between perimeter fluorescence properties and the ageing method; band widths and intensities appeared to depend on a combination of pigment composition and deterioration environment, with patterns difficult to identify.

Volumetric changes were suggested by the formation of voids within samples and by surface contraction. Voids were prevalent through the upper half of priming layers in samples of Yellow ochre, particularly those subjected initially to photochemical deterioration. Both primed and unprimed layers of Cobalt blue were also prone to voiding. Samples of Cremnitz white developed horizontal (intralayer) cracking in the early stages of thermal deterioration.

Contraction was evident when sectioned samples developed a concave presentation surface. Samples had all been surfaced uniformly using Micro-mesh® cushioned abrasive (silicon carbide) cloths on an automatic polishing wheel without lubricant, so preparation was unlikely to have contributed to the changes. Unaged control samples were generally the most unstable. The exceptions were Cremnitz white, unprimed samples prepared with Titanium white, and samples containing French ultramarine; the first being low in medium, the last two containing proportions of a magnesium aluminium silicate extender. Paint films were similarly prone to planar deformation in the initial stages of thermal deterioration, or when thermally deteriorated following photochemical deterioration.

### Response to Rhodamine B

Embedded samples were observed for their response to Rhodamine B (RHOB), applied as a 0.1% weight/volume solution in 9/1 xylene/ethanol by volume. A drop of RHOB was delivered to the section and then immediately blotted off. Samples were left open to the air for a minimum of ten minutes before residual RHOB was cleared by wiping the surface with tissue moistened by a few drops of xylene. Sections were coverslipped with Stoddard Solvent, ex-

amed with both broad band ultraviolet excitation and green excitation, and photographed.

The response of a paint film to RHOB will generally decrease as deterioration of the oil media progresses (8). Decreasing RHOB fluorescence in the paint standards generally corresponded to increases in autofluorescence and brittleness apparent in the same samples; thermally deteriorated paint films incorporating Cremnitz (lead) white recorded progressively weaker responses to the application of RHOB, whereas the RHOB response of Yellow ochre samples did not vary significantly throughout the deterioration programs. The phenomena where bands of the surface, perimeter and interface fluoresced differently to the rest of the sample did not necessarily correspond to features observed with autofluorescence and were not always consistent between samples embedded and sectioned after differing periods of ambient storage. Similarly, minor shifts in the intensity or hue of autofluorescence which accompanied the transfer of samples between different ageing environments were frequently not accompanied by corresponding variations in RHOB response.

#### ■ Cremnitz white

Samples containing Cremnitz white were most dramatically deteriorated thermally, decreasing the triglyceride content of the oil to such a degree that films of Cremnitz white and Ivory black/Cremnitz white became virtually unresponsive to RHOB in their most deteriorated state. In contrast, photochemical deterioration caused very little change in RHOB emission, even when followed by exposure to elevated temperature.

Cremnitz white paint films appeared to reach a threshold after the second sampling stage of thermal deterioration so that continued deterioration, whether by thermal or photochemical means, greatly diminished RHOB response. This corresponded to a significant increase in brittleness at a macroscopic level.

Paint films containing Cremnitz white were also easily affected by solvent on application of RHOB, with resultant irregular uptake, frequently in horizontal channels through the paint film. The same samples had attracted air bubbles to their surface while being embedded in polyester resin in preparation for sectioning; this was not generally apparent with other sample types.

#### ■ Titanium white

Samples containing Titanium white responded quite consistently and intensely to RHOB throughout the deterioration programs, even after thermal ageing. The most degraded samples registered a reduced RHOB response at their perimeter, although this feature was less significant in a second range of samples taken from the same source but embedded and sectioned several months after the completion of deterioration programs. However, samples with Cobalt blue were significantly affected by solvents on application of the RHOB and results were difficult to interpret.

#### ■ French ultramarine

Control samples of French ultramarine prepared with Cremnitz white had a lower intensity of response to RHOB than samples prepared with Titanium white, and also appeared to fluoresce 'yellow' rather than the 'orange' of the latter. Samples containing French ultramarine responded quite intensely to RHOB, with negligible variation between stages of deterioration or exposure to different deteriorating environments other than those arising from differences between Cremnitz and Titanium whites, most evident with thermal exposure. Thermal exposure following photochemical deterioration caused a minor reduction in RHOB fluorescence.

#### ■ Ivory black

Samples containing Ivory black exhibited behaviour consistent with French ultramarine on thermal deterioration, with samples prepared with Cremnitz white showing a negligible RHOB response in their most deteriorated state.



However, photochemical deterioration appeared more advanced than had been the case with French ultramarine, and samples prepared with Titanium white then registered a reduced RHOB response after subsequent thermal exposure.

#### ■ Primed Ivory black/Titanium white

Primed samples of Ivory black/Titanium white exhibited similar perimeter banding phenomena to unprimed paint films, but with reduced RHOB response in the paint layer at the interface with the priming. Thermal deterioration resulted in a decreased RHOB response along the upper surface of samples, and this became more distinct after subsequent photochemical deterioration. Initial photochemical deterioration did not promote this feature, nor second stage thermal exposure. Perimeter banding was not observed to diminish after a period of ambient storage as had been the case with unprimed samples.

#### ■ Primed Yellow ochre

Samples of Yellow ochre generally responded to RHOB with an intense, uniform fluorescence. The presence of a priming layer resulted in some variation in this response at the interface, although the most significant effects were evident in the priming layer itself. Physical differences between the samples complicated interpretation of RHOB uptake at the paint/priming interface, most obviously when voids were present. Samples embedded several months after the completion of accelerated deterioration generally exhibited a less intense RHOB emission in the priming layer than did samples examined without a period of ambient storage, so the most significant difference over time was the relative intensities of fluorescence in paint and priming.

#### ■ Primed Cobalt blue

Samples of primed Cobalt blue/Titanium white exhibited a band of intense RHOB fluorescence at the upper paint surface in Control and photochemically deteriorated states. The most advanced stages of thermal deterioration induced a band of intense RHOB response at the upper priming surface, with a band of greatly reduced RHOB fluorescence in the paint layer immediately adjacent, and also at the upper paint surface. Samples transferred from thermal to photochemical deterioration programs exhibited the same response to RHOB as samples maintained under elevated temperature, although the fluorescence shifted from orange to yellow.

### Discussion and conclusions

Material exuded from unvarnished oil films is known as efflorescence. Perry refers to analysis which has shown various efflorescences to consist of a variety of organic materials and degradation products migrating from paint and ground layers often with traces of inorganic pigments and extenders (9). No comparable analysis was undertaken on the paint films in this study. However, many of the features observed in samples in cross-section seem to indicate that components of the oil media are mobile and migrating within paint layers, and that this movement is to some degree dependent on deterioration and the environment.

Microscopical examination of paint cross-sections showed that many samples exhibited different autofluorescence properties at their perimeter or their interface with a priming layer as compared to the bulk of the sample. Autofluorescence and the response of samples to RHOB was not uniformly consistent, however trends emerged according to pigment composition and deterioration environment. Autofluorescence and RHOB response also intensified or diminished with time, both throughout ageing and in the subsequent months of storage in ambient conditions, consistent with changing molecular distribution within samples. The components with greatest mobility within a paint film are likely to be short chain molecules, such as those produced by random chain scission degradation reactions. The rate at which such reactions occur among other competing reactions during deterioration of an oil paint film will depend on the type and condition of oil that is present (i.e the distribution of unsaturated fatty acid), the pigment/drier formulation and concentration, and the prevailing exposure

environment (10). It is for these reasons that such variation occurs in the RHOB response of different samples.

Exposure of samples to elevated temperatures or intense light will result in accelerated formation of degradation products. Short chain, polar molecules will tend to migrate away from the increasingly saturated, non-polar oil film bulk, i.e. to the oil/air interface or possibly towards the Melinex substrate which is also polar by comparison. The propensity for these molecules to accumulate at, or evaporate from, the perimeter of the sample will depend on its composition and molecular mobility, surface area, and ambient temperature and relative humidity. In a significant number of cases, samples embedded in polyester resin immediately following ageing appeared to have a perimeter which the resin readily wetted; it has not been determined whether this is due to medium depletion rendering the surface porous, or a concentration of short chain polar molecules for which the resin has an affinity. In either case, the phenomenon is less significant when samples have been stored under ambient conditions for several months prior to embedding.

The argument for exaggerated porosity at the surface of thermally aged samples is supported by the level of surface contraction observed in primed samples of Yellow ochre. Paints were applied to prepared films of Foundation white just one day after the primings had been removed from the 'drying' oven. Of the three paints with priming, Yellow ochre has the lowest affinity for oil but the highest ratio of oil to pigment. Therefore, it is likely to lose the most significant proportion of medium when applied to an absorbent substrate. The rapid development of cracks in this artists' quality Yellow ochre suggests atypically high absorbency in the priming.

The application of oil paint to the priming also accounts for some of the initial fluorescence phenomena observed at the paint/priming interface of samples. In the case of Yellow ochre, the quantity of oil transferred could initiate swelling in the upper band of the priming; subsequent distribution of oil throughout the priming could then account for the voids which appear. Primed samples of Cobalt blue/Titanium white also initially respond to RHOB in a manner which suggests oil is being drawn into the priming from the narrow band of paint with which it is in contact. The distinctive 'banding' pattern of the RHOB response becomes less distinctive as the samples age; such deterioration will be influenced by the proximity of a lead containing layer but it also suggests that oil medium continues to migrate through the film.

### Acknowledgements

I would like to acknowledge the advice, encouragement and assistance of staff in the Tate Gallery Conservation Department, particularly Joyce Townsend, Stephen Hackney, Anna Southall and Roy Perry. My special thanks also to the Queensland Art Gallery for its ongoing support. My work was aided financially by the Queen Elizabeth II Silver Jubilee Trust for Young Australians, Australia Council, The British Council and the Queensland Art Gallery.

### Materials

Rhodamine B (RHOB).  $C_{28}H_{31}ClN_2O_3$ . BDH Merck Company, Ltd., Product Code 13111-34142.

Winsor & Newton artists' oil colours. Colart Fine Art & Graphics, Whitefriars Avenue, Wealdstone, Harrow, Middlesex HA3 5RH, United Kingdom.

Micro-mesh®. Cloth-backed, silicon carbide abrasive. Micro-Surface Finishing Products, Inc. Box 818, Wilton, Iowa 52778, USA.

### Notes

1. Research proposal initiated in consultation with Richard Wolbers: to investigate applications of Neutral Red and the influence of age of an oil paint film on its response to the fluorochrome Rhodamine B.
2. Pigment and medium specified by Winsor & Newton. Supplementary inorganic





- analysis undertaken by Joyce H. Townsend using energy dispersive x-ray analysis, corroborated with x-ray diffractometry for (i), (ii) and (viii).
3. Cobalt undetectable by EDX. Pigment information supplied by Winsor & Newton.
  4. Paint was spread onto Melinex by drawing a microscope slide across two parallel lengths of tape to form a layer of approximately 70µm thickness. Duplicate samples of each paint type were allocated for the different deterioration regimes.
  5. Example: Jane L. Down, "The yellowing of epoxy resin adhesives: report on high-intensity light aging," *Studies in Conservation* 31 (1986): 159-170. E. René de la Rie, "Photochemical and thermal degradation of films of dammar resin", *Studies in Conservation* 33 (1988): 53-70.
  6. Example: Robert L. Feller, "Some Factors to be considered in accelerated-aging tests", *AIC Preprints Vancouver BC 1987*: 56-57.
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# Working Group 7

Wet Organic Archaeological Materials

Matériaux organiques archéologiques  
gorgés d'eau





## Abstract

Tetraethylene glycol (TEG) was aged at 70°C in a stream of gas. TEG is stable in nitrogen but decomposes in dry air. Water vapour in the air reduces the rate of degradation. Copper acetate and ferric chloride inhibit degradation, and nickel sulfate accelerates degradation. The main degradation product is of higher molecular weight. The sensitivity of TEG, and therefore presumably of all polyethylene glycols, to small alterations in the chemistry of its environment casts doubt on the wisdom of accepting PEG impregnation as a standard preservation technique for waterlogged wood.

## Keywords

Tetraethylene glycol, polyethylene glycol, thermal degradation, gas chromatography

## The Thermal Degradation of Tetraethylene Glycol, a Model Molecule for Polyethylene Glycol

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## Introduction

In a previous article we demonstrated that PEG 4000, a synthetic polyethylene glycol wax which is extensively used for the stabilisation of waterlogged wood, suffered degradation through heat treatment (1).

To examine the degradation more systematically we chose a model molecule, tetraethylene glycol (TEG). This molecule is small enough that both it and its degradation products can be analysed directly by gas chromatography (GC) and by mass spectrometry (GC/MS). TEG is one of the two main oligomers in the commercial product PEG 200. TEG was heated to 70°C while a stream of gas was blown through it. We measured the decomposition rate of pure TEG in nitrogen and in air at different relative humidities. We also bubbled air at 75% RH through samples of TEG contaminated with 10mM of  $\text{FeCl}_3$ ,  $\text{Cu}(\text{CH}_3\text{COO})_2$  and  $\text{NiSO}_4$ .

## Materials and methods

The chemical used as a model for the degradation of PEG is tetraethylene glycol (TEG, CARN 112-60-7). The experiments were performed in an oven at 63°C. The oven contained a flask of water through which the gas was bubbled. The reaction vial was 5 ml 33-expansion borosilicate glass from Wheaton. 2.0 ml of TEG was put in the vial which was then placed in an aluminium block sitting in the oven. The block was heated to 70°C. The saturated gas stream from the water flask at 63°C was further heated to 70°C in a coil in the aluminium block. This lowered the RH to 75%. The gas then bubbled through the TEG. For the dry experiments the water flask was empty and for the 5% RH experiments the water flask was outside the oven.

All tubing was 1/8" and 1/16" Teflon. The nitrogen and air were passed through Molecular Sieve 3A and activated charcoal (Merck 2514 & 5704). The air pressure was set at 170 kpa. The flow was controlled by restrictors made of polyimide-coated fused silica with an internal diameter of 60  $\mu\text{m}$  (J&W Scientific, Folsom, California). The flow rate is determined by the Poiseuille equation: 1, 2, 4 and 10 cm lengths give a flow of 10.0, 5.0, 2.5 and 1.0  $\text{cm}^3/\text{min}$ , respectively, at this pressure.

We first measured the degradation rate of TEG in the reaction vials with different air flows in order to find the minimum air flow that ensured the maximum reaction rate. At air flow rates of 10 and 20 ml air/minute, the slope of the curve, i.e., the degradation rate, is the same, whereas at 5 ml/min the degradation rate is somewhat lower. We chose 10 ml/min for all the experiments. Nitrogen was also tested at this bubbling rate. TEG showed no degradation under these circumstances.

For the analysis, 2  $\mu\text{l}$  aliquots were withdrawn from the reaction flask and transferred to a vial with 1.0 ml acetone spiked with 0.5 mg methyl palmitate as internal standard. The samples were analysed by a Varian 3500 Gas Chromatograph. The experimental parameters were as follows: carrier gas  $\text{H}_2$ , initial column temperature 110°C, hold 0.5 min, ramp rate 40°C/min to 175°C, hold 0.3 min; injector 275°C, split 25, column flow 2.0 ml/min; detector 230°C, att. 32; and column BP-5, 4 m long, 0.32 mm i.d., coating 0.25  $\mu$  (J&W Scientific).

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Analysis of the degradation products was performed on a Varian Saturn II GC-MS. The GC carrier gas was helium. The experimental parameters for GC were as follows: initial column temperature 110°C, ramp rate 10°C/min to 210°C, hold 3 min; injector on column, initial temperature 60°C, ramp rate 200°C/minute to 275°C, hold 12 min; transfer line 230°C; and column 20 m BP-5, 20 m long, 0.18 mm i.d., coating 0.40  $\mu$  from J & W Scientific. The experimental parameters for MS were as follows: manifold temperature 220°C, electron emission current 10  $\mu$ A, scan segment from 50 to 399 amu, and 1 scan/sec.

### The reaction kinetics

Figure 1 shows the effect of relative humidity (RH). Note that even 5% RH noticeably protects the TEG and 75% RH reduces the decomposition rate by about 30%. At this RH the TEG contains about 27% water.

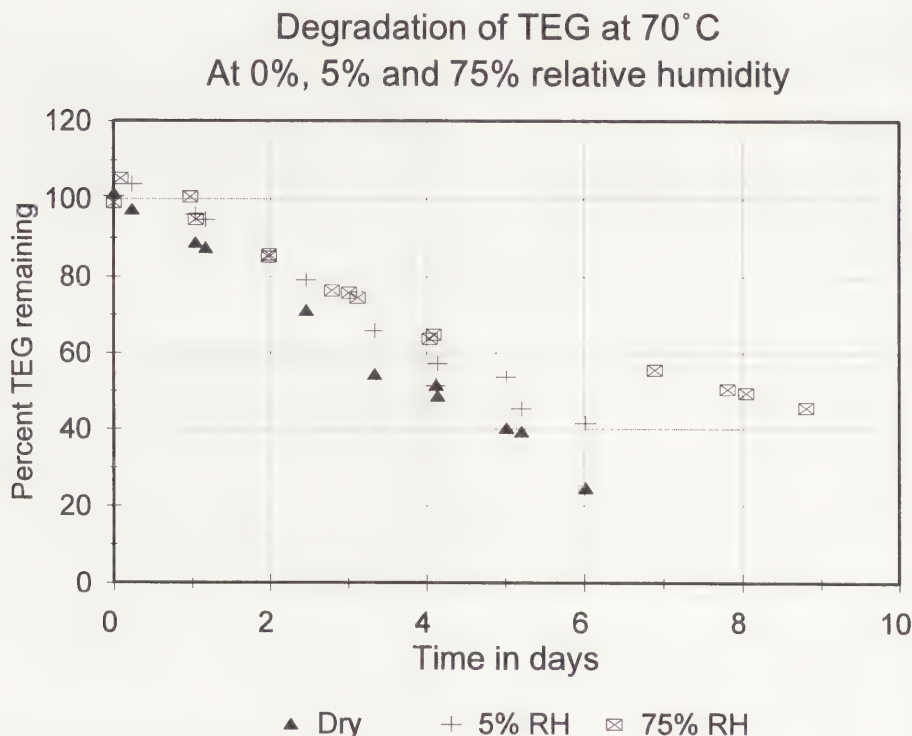


Fig. 1: The decomposition rate of TEG at 70°C in air at different RH values.

Figure 2 shows the effect of 10 mM of metal salts added to the TEG. Minor amounts of ferric chloride and of copper acetate completely protect against oxidation, while nickel sulfate accelerates the reaction.

Figure 3 shows the decomposition of TEG in dry air at 40°C, compared with the rate at 70°C. After one week of apparent stability the TEG begins to decompose.

### The reaction products

The reaction products from the degradation have been examined by GC-MS. Figure 4A shows the chromatogram from fresh TEG and figure 4B shows the chromatogram of TEG which has been treated with dry air at 70°C for one week. The primary degradation product comes out at 524 seconds. This component comes out later than the TEG peak at 458 seconds, which indicates that the degradation product results from an addition to the TEG molecule. This is supported by the fact that we found in the mass spectrum of the degradation product an ion at 223 atomic mass units (amu) and probably another ion at 239, whereas in TEG we found a molecular ion at 195 amu ( $M+1$ ). A third component at 580 seconds appears as degradation proceeds. It has more or less the same fragmentation pattern as the peak at 524 seconds and is probably a result of further reaction with this primary degradation product. The degradation products are presently under examination.



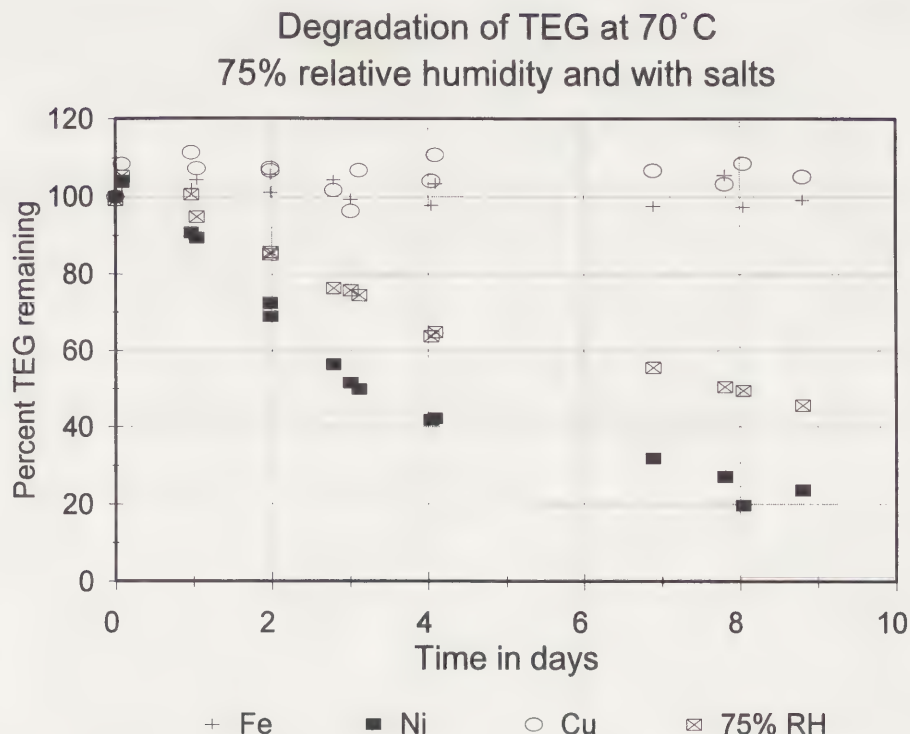


Fig. 2: The decomposition rate of TEG contaminated with metal salts at 70°C in air at 75% RH.

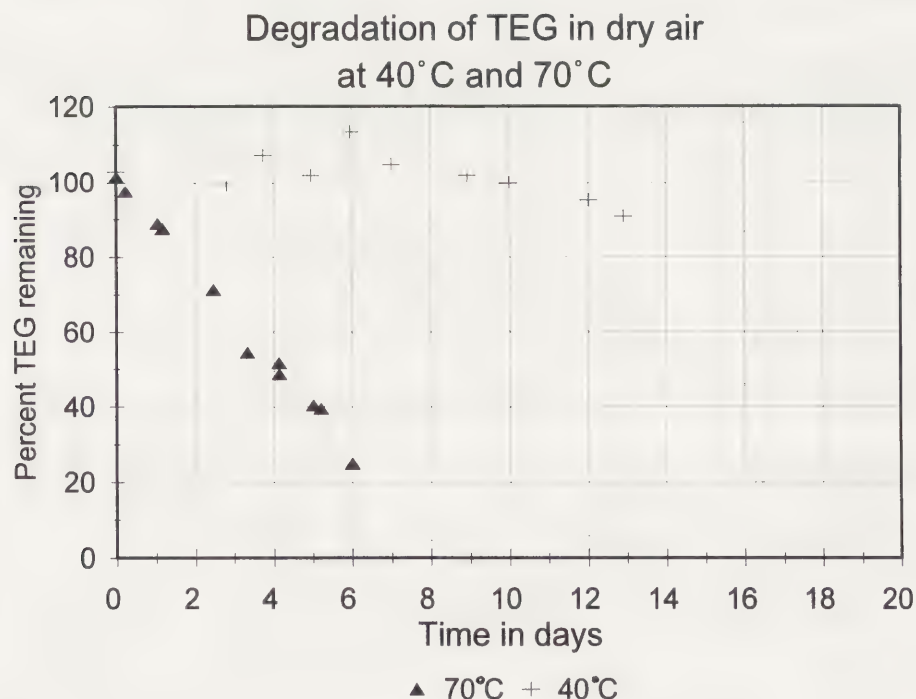


Fig. 3. The decomposition of TEG in dry air at 40°C and at 70°C.

### Discussion

Polyethylene glycol (PEG) is a material of vast industrial importance. Besides its use in the conservation industry, it is used in large amounts in medical, pharmaceutical and cosmetic formulations, in the battery industry and in chromatographic applications. However, most of the research on the stability of PEG has been done under severe conditions: ultrasonic radiation (2), gamma radiation (3,4), under high oxygen pressure at 120°C (5,6) and at high temperatures (280–420°C) with or without oxygen present (7,8,9). At high temperatures (200–300°C) the degradation of PEG takes place in days or hours, even at ppm and ppb levels of oxygen (10,11). Riecke and coworkers demon-

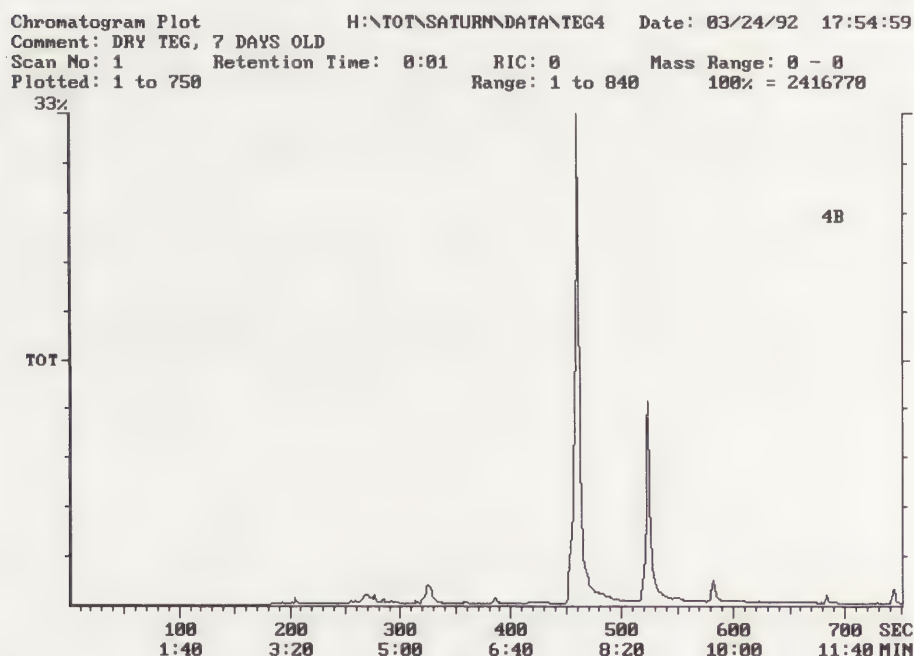
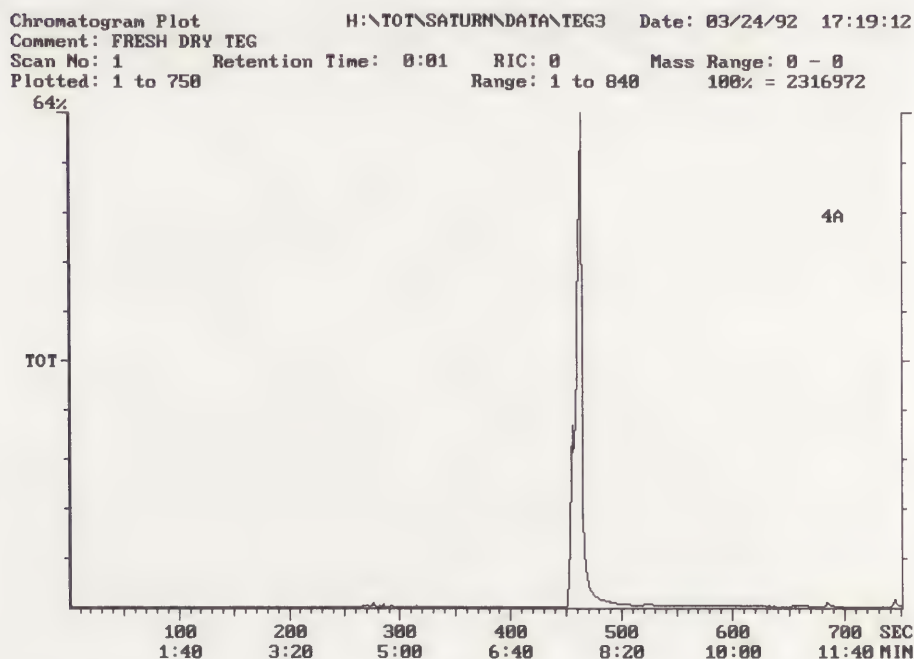


Fig. 4. (A) Gas chromatogram of fresh TEG, and (B) TEG after exposure to dry air at 70°C for seven days.

strated in the fifties that organic materials containing ether groups suffer degradation through peroxide formation next to the ether bond (12,13). At relatively low temperatures (120–160°C) in pure oxygen, the main degradation is caused by peroxide formation, and the degradation products are water, carbon dioxide, formaldehyde, acetaldehyde, methylformate and ethylformate (14). This is generally in agreement with other studies of the oxidative degradation of PEG (5–9,15). The results seem to support peroxide formation and degradation through a radical mechanism. McGinity et al. have demonstrated that peroxides are found in all commercial PEG products and that removal or inhibition of these peroxides stabilises the product. Water seems to inhibit the peroxide formation (16). Inorganic salts have previously been demonstrated to have a stabilising effect on the oxidation of PEG (7).

In work more directly related to conservation, de Witte et al. showed decomposition of PEG 4000 in water during a two year treatment of a wooden boat at 65°C (17). The decomposition appears to accelerate in the later stages when the PEG bath was nearly free of water. There was approximately 20% degra-



dation of the PEG during the first 22 months during which the PEG concentration increased from 10% to about 80%. During the next six months, while the PEG became water-free there was a further 15% degradation. Recently, de Simone et al. have performed a series of experiments with PEG 200 and hexaethylene glycol at 80°C (18). The main conclusions were that fast degradation could be seen with dry glycol whereas water slowed degradation. Gallic acid and iron salts stabilised the glycol. These experiments were performed in sealed ampoules which lost oxygen during the exposure, and the results cannot be directly compared with ours.

Our earlier experiment on commercial PEG showed degradation to lower molecular weight compounds (1). This we now attribute to the influence of minor impurities. In the experiments on pure TEG reported here the higher molecular weight degradation product seemed relatively stable. In early experiments, however, with stainless steel used as the nozzle, we have seen results ranging from almost complete stabilisation of the TEG in the presence of water to a degradation proceeding as fast as in dry TEG. No addition product was found in this case but brown deposits were found on the stainless steel nozzle which also showed light signs of corrosion. We believe that the deposits or the corrosion products from the stainless steel have influenced the stability of the addition product.

### Conclusions

We have found that tetraethylene glycol can decompose disturbingly fast in the presence of air at relatively low temperatures. In less than a week in dry air at 70°C only 30% of the TEG remains. The main reaction product of this fast degradation is probably an addition product, because it comes out later than TEG in the gas chromatogram (Fig. 4) and shows a higher molecular weight in the mass spectrum.

These experiments on tetraethylene glycol, the previous results from polyethylene glycol and results extracted from the literature show without doubt that polyethylene glycol is not inherently stable. In the presence of air it decomposes. This decomposition is markedly slowed by the presence of iron and copper, somewhat slowed by water, and accelerated by nickel. These observations are compatible with anecdotal evidence for the erratic behaviour of PEG in conservation. There have been reports of surface stickiness, whitening of surfaces (probably through phase separation), instability in the impregnation bath, and deliveries of unused but already decomposed batches of PEG. These reports, together with many examples of apparently satisfactory stability of treated objects, confirm the sensitivity of PEG to stabilisation or destabilisation by subtle changes in its chemical environment.

Some of the degradation products that have been reported are toxic. There is a threat to the health of conservators from the unpredictable risk of rapid breakdown of PEG during the conservation process.

We have found a degradation path of tetraethylene glycol which is different from the previously described peroxydation of ethers (11) which leads to scission of the ether bond and the formation of smaller degradation products (14). This degradation can be stabilised or destabilised but at this stage it is difficult to envisage a reliable stabilisation technique.

PEG impregnation has achieved the status of a standard conservation procedure, almost universally used in the treatment of waterlogged wood. This is quite clearly undeserved. We are not suggesting that all wood treated in this way will fall apart in a few years. Air can only diffuse slowly through the solid PEG on the surface of the wood. Traces of iron may further stabilise the PEG. It seems unwise, however, to rely on a basically unstable material for a process designed to protect wooden relics for a very long time.

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## Abstract

Several case studies are described of the restoration of dried-up wooden archaeological finds showing deformations due to shrinkage, collapse, and mechanical damage. Such objects can be waterlogged again, the wood plasticized and reshaped, shrinkage swollen again, and the corrected, wet objects stabilized with well-established methods of waterlogged wood conservation.

## Keywords

Turned woodware, waterlogged wood, deformed wood, plastification, stabilization, shrinkage

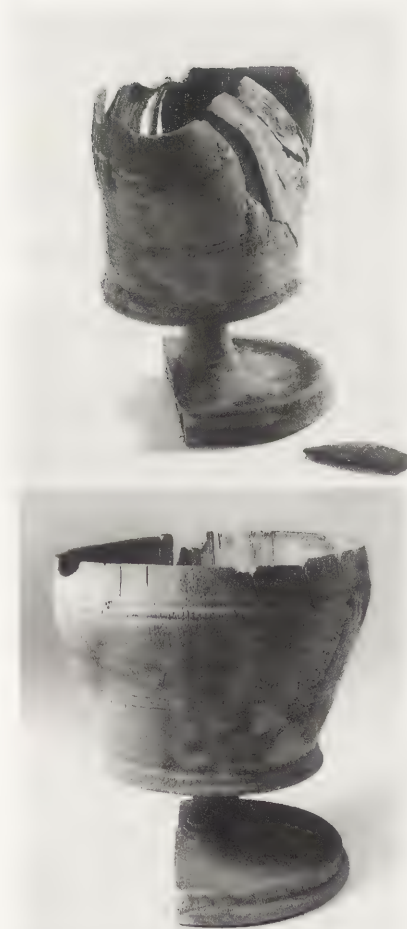


Figure 1. Wooden medieval goblet from a garbage pit. Dried and distorted after excavation, and restored to its original shape. Photograph by E. Laszka, German Maritime Museum.

## Restoring Deformed Fine Medieval Turned Woodware

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## Introduction

The medieval horizons under the old centres of many German towns yield a wealth of wooden objects. Especially rich are the deposits in garbage pits. These are brick- or wood-built wells into which household garbage was thrown and toilets emptied. The resulting anaerobic and moist milieu preserved many organic materials in a nice if smelly state.

Wooden household objects like stave-bound jugs, beakers, plates, small barrels, lathe-turned bowls, plates, boxes, jars, and wonderful goblets have been excavated during the last decades. Until recently, only few conservators knew how to treat these finds and, therefore, most of the objects were stored or exhibited in whatever form they would develop upon air drying.

However, many of these distorted objects can successfully be restored to a much better appearance (fig. 1). This paper deals with the two main damages occurring in the old finds: mechanical damage due to earth pressure and deformation caused by shrinkage and collapse of tissue of the once waterlogged wood as it dries.

## Preliminary experiments

The permanent correction of a mechanical deformation can be based on the fact that the lignin component of wood plasticizes at temperatures above 80–100°C and stiffens again on cooling. To establish the optimal temperature, small boards of several hardwoods of 3 mm thickness were steam-heated to 100, 120, and 140°C. The boards were then either bent over a cylinder of 90 mm diameter or twisted 90–180°, and fixed in this position during cooling and air-drying. Heating to 100°C proved to be the best procedure; at higher temperatures some samples buckled at the growth ring borders when bent and split lengthwise on torsion (fig. 2).

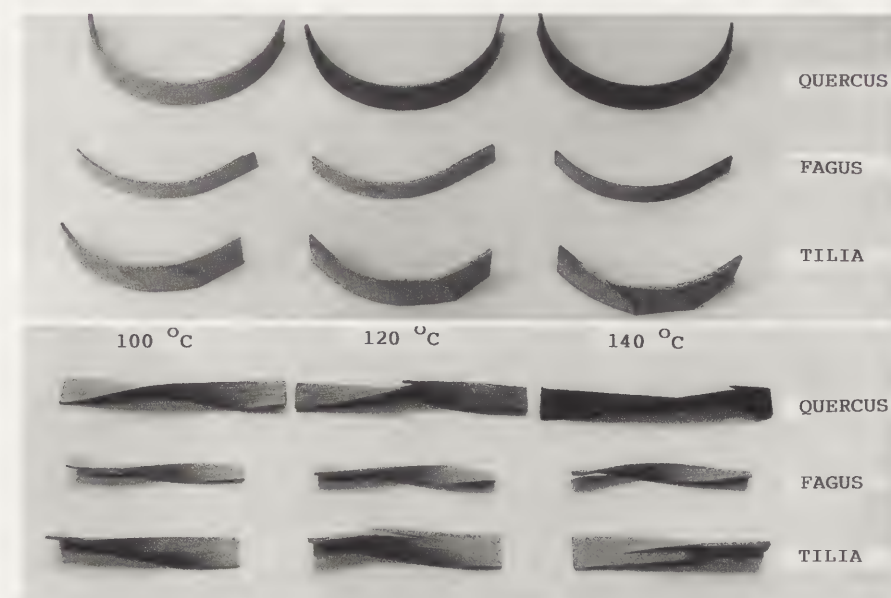


Figure 2. Thin stripes of wood steamed and bent or twisted at different temperatures, and cooled in fixed positions.

“Shrinkage” of wood means a contraction of a piece of wood due to the evaporation of water from the cell walls, a process in which the structure of cell walls and of the whole tissue keeps its integrity. This process is reversible on

rewetting ("swelling"). "Collapse" means the breakdown of the cellular structure in heavily degraded wood during, and caused by, the evaporation of water from the weakened tissue. Collapse is associated with a significant contraction of the wood. This process is not reversible, as the degraded cell walls have lost the elasticity to spring back into their original shape when rewet.

Many archaeological objects contain heavily degraded and less degraded wood tissue side-by-side. In dried objects the dimensional contraction may thus be due to both shrinkage and collapse. As the shrinkage is reversible, it is worthwhile to try and rewaterlog the wood and to stabilize the swelling thus achieved. The swelling may be enhanced by using a slightly alkaline solution, e.g., 1% NaOH.

Fig. 3 shows the results of a series of swelling experiments with small cross sections of woods of various degrees of degradation. Even the evidently collapsed air-dry samples of oak, hazel, and beech are swollen considerably with 1% NaOH, whereas the elm wood has not responded at all.

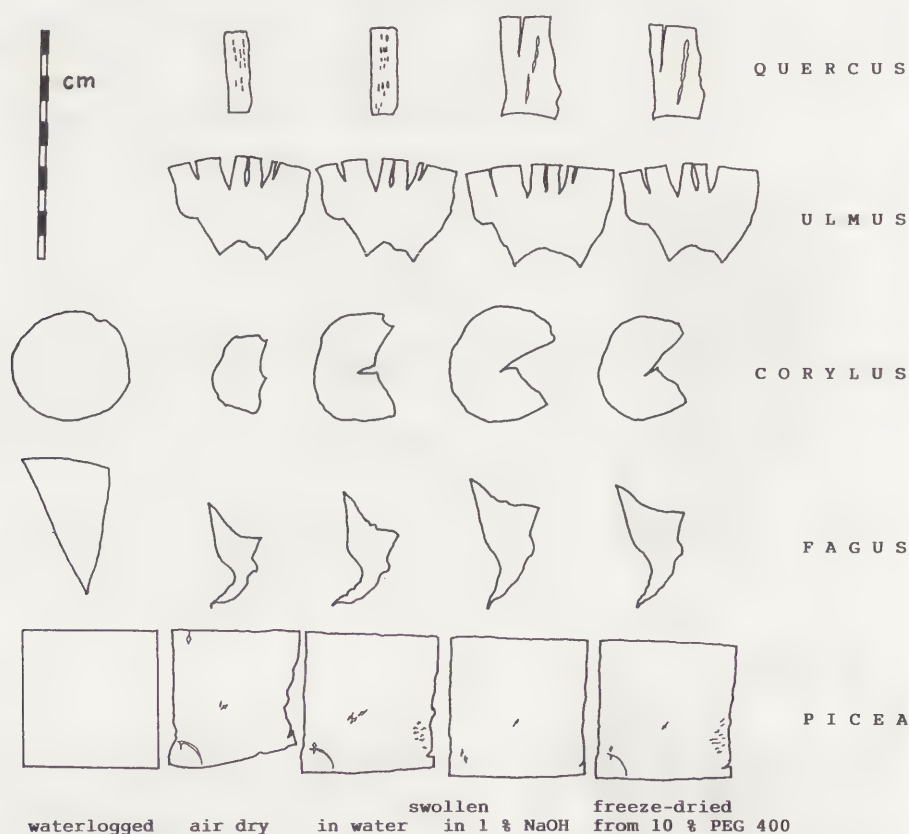


Figure 3. Reactions of cross-sections of degraded waterlogged wood to air-drying, re-swelling, and stabilization of the swollen state.

### Restoration of a crushed bowl

A late medieval ornamental bowl was excavated in Freiburg in a heavily crushed state, and then stored away for years. The walls of the body of the bowl—very uniformly 4 mm thin—showed all sorts of cracks and fractures, along the wavy grain and across the grain (fig. 4). However, the yew wood (*Taxus baccata* L.) gave no signs of biological or chemical degradation; it was hard and rigid.

The restoration of this bowl involved several steps: cleaning, correction of non-separating fractures, correction of deformed spherical parts of the bowl, glueing of fractures (some were very complicated), and replacement of missing parts to stabilize the final shape.

Some dirt that was still adhering came off easily when the bowl was boiled in distilled water for five minutes. This also softened several provisional old glueings. The bowl fell apart into eight pieces, and the glue could then be removed with a scalpel. From the largest part, the dimensions of the inner contour could be measured. A wooden core was fabricated on a lathe over which the distorted



Figure 4. Medieval wooden bowl crushed by earth pressure. Separating and non-separating fractures distort the spherical body of the bowl.



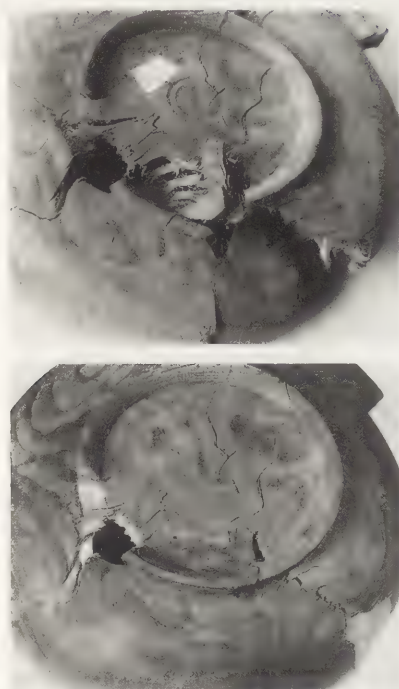


Figure 5. Cracks, cross-grain ruptures, and shear-fractures in the bottom of the bowl from figure 4, before and after restoration.

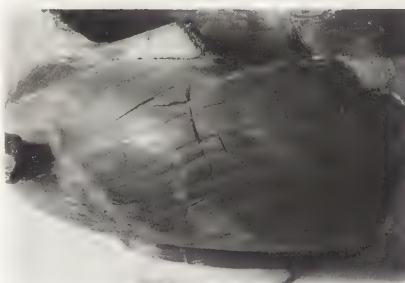


Figure 6. Same area of the bowl as in figure 4 after reshaping and closing of cracks.

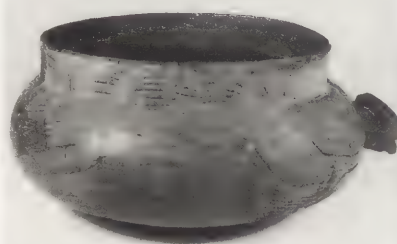


Figure 7. The bowl after restoration.

fragments were to be corrected and reassembled, based on the inner core measurements of the bowl.

To avoid the natural shrinkage of up to 5% occurring on the air-drying of the sound steam-treated wood after the reshaping, the fragments were artificially waterlogged in several vacuum/ambient air pressure cycles, and then soaked in a 10% solution of PEG 200 (polyethylene glycol with molecular weight 200) for six weeks. Previous experiments had shown that even with subsequent air-drying, this treatment would reduce shrinkage to 0–1 % without affecting the dry appearance of the wood (1). The infiltration of the wood with PEG 200 would probably also assist in its plastification.

While still in the PEG solution, the fragments were heated to 100°C for 10 minutes and then pressed in shape over the wooden core. During this process it was necessary to correct the contours of the core until the fragments fitted together in the only possible way. Intermediate reheating of fragments was necessary, and sometimes considerable pressure had to be applied to form them. The fragments were bandaged around the fabricated core and allowed to dry for two days.

The fragments were then glued together on the core, which previously had been cut into segments so that it could be extracted from within the reassembled bowl at the end of the treatment. A quick-setting polyvinyl acetate glue ("white glue") was used, together with a lot of clamps, as this glue can be removed again with hot water.

Not all cracks and fractures could be closed totally. But then total closure would be next to impossible with most frayed cross-grain fractures, even in simple woods. The comparison of the worst fracture areas shows what repair was possible (figs. 5 and 6).

The reshaped and reassembled bowl still held considerable stress, and the coherence of the spherical form was broken due to some missing parts. This made it necessary to fill in these gaps. The two-component epoxy resin Araldite (SV 427 and HV 427, Ciba-Geigy) makes a hard and porous polymer which can be cut, sanded, painted, and polished like wood and which sticks sufficiently well to dry wood.

The restored bowl still shows its original silky gloss, the result of a very fine sanding, even after the rather crude treatment administered to give it back its original shape and splendour (fig. 7). It belongs to a class of ornamental bowls called "Scheuer" in Southern Germany that were once regarded valuable enough to be sometimes mentioned as separate items in contracts of inheritance.

### Restoration of objects with shrinkage and collapse damages

Shrinkage of the slightly degraded and once waterlogged wood was the cause for the distortion of a very delicate medieval wooden goblet from Lubeck (fig. 1). The wood is maple (*Acer* species). Local collapse was evident in the formation of honeycomb surface cracks. The goblet was covered with very resistant dirt and the smell of the goblet after boiling in water revealed where it had spent the last centuries. To remove dirt and staining from the wood it was necessary to boil the goblet in a strong surfactant solution and then to immerse it for three hours in a 3% solution of hot (90°C) EDTA-Na<sub>2</sub>. The latter treatment restored the wood to its original light colour. Two days of washing in hot water finished the process.

During the cleaning operation some provisional glueing dissolved, and six smaller fragments came loose. The hot cleaning process rendered the goblet very soft and pliable. The correct inner contour of the bowl was measured and a wooden core made to fit into it. The bowl and the loose fragments were affixed to the core with gauze. The now waterlogged goblet was then stabilized as if it were a conventional wet, wooden archaeological object, except for a slight modification. The butanol/PEG method was developed by Brorson Christensen in the sixties for the conservation of the Danish Viking ships from the Roskilde Fjord



(2). The water in the wood was exchanged for tertiary butanol in three steps, then 15% PEG 400 and 40% PEG 3000/4000 were added to the last bath of 100% butanol. After 10 weeks of infiltration with PEG sublimation of the butanol was effected under vacuum at ambient temperature (the freezing point of t-butanol is 25°C). The fragments were glued in place with an isocyanate glue, as vinyl acetate does not bind well on wood treated with higher amounts of PEG. After the removal of the fabricated wooden core, the goblet appears restored nearly to its original form (fig. 1). On some areas the gauze left imprints in the soft wood surface; therefore, bandages of a much finer weave would have been advisable (fig. 8).



Figure 8. Imprints from gauze bandaging on the surface of the goblet of figure 1.

After the restoration, the wood is not as hard as it was before treatment and does not "sound" when struck. Probably the PEG 400 should have been omitted in this case of a degraded and easily permeable wood.

The potential of swelling and stabilizing treatments for the restoration of shrunken wooden objects is demonstrated best in the restoration of four sturdy soup bowls, again excavated from a garbage pit of a former Augustinian monastery in Freiburg many years ago, and a small cylindrical box from the city of Konstanz; all the artifacts are made of maple wood.

Shrinkage after the excavation had caused the small bowls (14 cm in diameter) to crack radially and to take on a typical "boat" shape. In addition, one bowl had been severely bent and partly broken over the edge of a brick by soil pressure

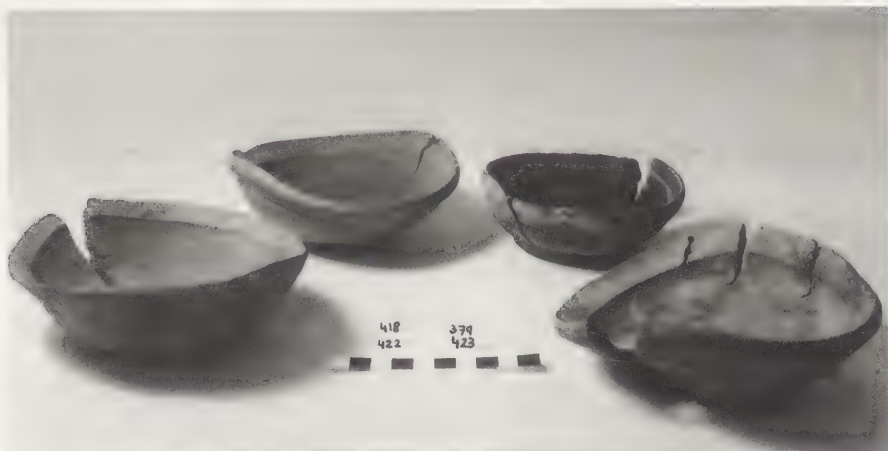


Figure 9. Late medieval eating bowls. Dried, cracked, and distorted after excavation, and reswollen and stabilized in their original shape.

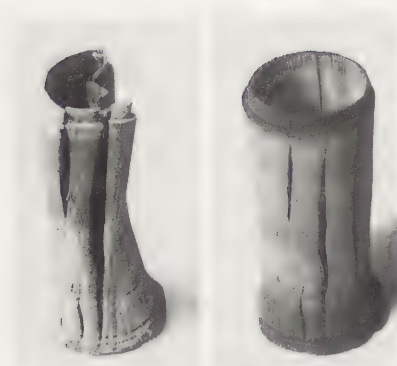


Figure 10. Cylindrical box from a garbage pit. Dried and collapsed after excavation, and reshaped and stabilized as far as possible. Collapsed tissue could not be reswollen.

in the pit (fig. 9). In the box, shrinkage and collapse had led to severe deformation (fig. 10).

Submerged by weights, the bowls were boiled in water for 10 minutes and then kept in the water during cooling. This effected a renewed waterlogging and softened the adherent dirt. After an additional 24 hours in hot water, the bowls swelled back to their original shape; the cracks closed and the rims returned to



the original plane. The bent-open bowl became so plasticized that it could be easily closed again.

The cylindrical box showed clear signs of wood cell collapse: honeycomb cracks in the bottom and large parts of the wall collapsed to half their original thickness. In addition, the wood was very light, soft, and spongy to the touch. Accordingly, the box did not swell in hot water, not even during 11 days in 1% NaOH-solution. But the wood became so pliable that the collapsed walls could be unrolled and bandaged with soft damask strips around an inserted wood cylinder. The alkali was washed out for three days in changes of hot water and the wood was then neutralized in 3% acetic acid for one hour. Two more days in hot water removed residual acid. A wooden core was made from waterlogged wood so that it would not swell further during the treatment of the box and split it.

A freeze-drying procedure after impregnation with 20% PEG 200 and 20% PEG 3000 was chosen to stabilize the swollen and reshaped objects. During the eight to nine weeks of PEG impregnation, the objects were kept fixed in their restored shapes to allow residual stresses in the wood to relax; the box was bandaged to its core, and each bowl was fixed between wooden rings to hold it together and to hold the rim in a level plane (fig. 11). After freezing the bandage around the box was removed to avoid the formation of stripes on the wood surface during the sublimation.

The appearance of the small cylindrical box after treatment is shown in Figure 10. Even if the cracks caused by collapse could not be closed totally, the shape is restored and the overall appearance is greatly improved; the object is again recognizable.

The freeze-drying process with the bowls broke down—typically—over the weekend. The vacuum collapsed, the half-dried bowls thawed and dried, reducing them nearly to their initial state through shrinkage. The whole process of swelling, fixing the correct forms, freezing, and freeze-drying was repeated. This time the bowls came out beautifully. The cracks stayed closed and were glued with isocyanate glue, and the rims stayed in plane after the removal of the clamping (fig. 9).

### Conclusion

Old wooden store-room “corpses” can very well be revived to waterlogged wooden objects, and as such can be restored to new splendour. Even delicate objects can take a lot of handling and treatment, as they are stronger and more patient than one might expect. It is worthwhile to attempt restoration treatment.

### Acknowledgement

My thanks go to the Deutsche Forschungsgemeinschaft for financial support of these investigations, and to Dr. Judith Oexle, Dr. Peter Schmidt-Thome, and Alfred Falk, M.A. for their confidence in my development of the described restoration methods on their most precious wooden objects.

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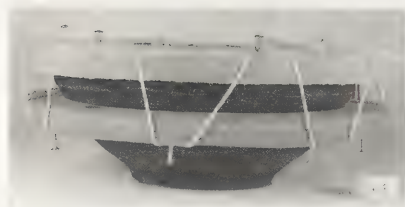


Figure 11. Re-waterlogged soup bowl clamped between wooden rings to fix it in its correct shape during the impregnation with polyethylene glycol.

## Abstract

The Department of Conservation has started to use two new methods for conservation of wet archaeological rope. Results from these methods show that the rope retains its original shape, colour and texture. The methods involve freezing the rope while it is still floating in liquid, in order to avoid compression caused by the rope's own weight. The first method is based on impregnating the rope with water-soluble materials, followed by freezing in organic solvent and freeze-drying at 50% relative humidity (RH). The second method begins with freezing the rope in pure water followed by freeze-drying at 50% RH. The dry rope is impregnated with polymers in non-polar organic solvent.

## Keywords

Archaeological rope, impregnation, freezing, freeze-drying

## Conservation of Wet Archaeological Rope

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### Traditional conservation method

Until recently, the standard method for the conservation of rope has involved five steps: cleaning before impregnation, packing before impregnation, impregnation, freezing, and freeze-drying.

Step 1. Cleaning of soiling with water, including dissolving iron salts with ethylenediaminetetraacetic acid (EDTA) followed by washing in water.

Step 2. The rope is placed on a layer of foam rubber on a piece of perforated masonite. Weak areas are further supported with small pieces of foam rubber. Finally, the whole rope is covered with a layer of foam rubber which is sewn to the masonite along the outlines of the rope (See fig. 1).

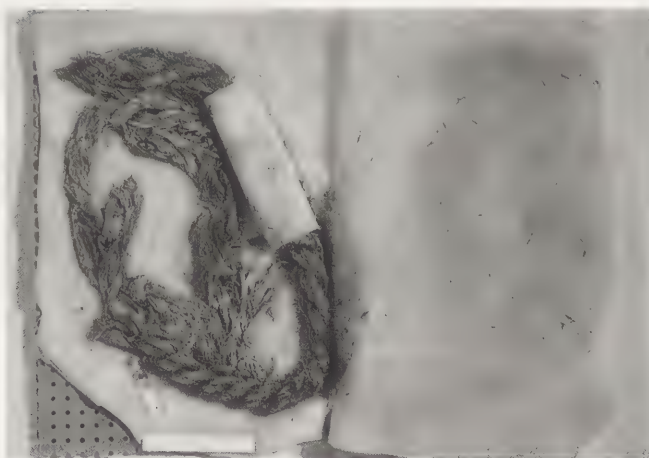


Figure 1. Traditionally packed rope.

Step 3. The rope is impregnated in a solution of 2% polyethylene glycol (PEG) in water (200–600) and 2% methylcellulose (Klucel E) for a fortnight.

Step 4. The packed rope is wrapped in a plastic sheet and frozen at  $-27^{\circ}\text{C}$ .

Step 5. The plastic sheet is removed and the packed rope is freeze-dried at 0.1 mbar, at a chamber wall temperature of  $20^{\circ}\text{C}$  and approximately 0.5% relative humidity (RH), until all ice is sublimed.

### Evaluation of the traditional conservation method

This method has several disadvantages. The packing is very laborious and time-consuming. The wide space between the holes in the standard masonite plate makes it difficult to make a tight support. As the foam rubber stretches when getting wet, it is necessary to keep it wet during the sewing. The wet foam rubber is very heavy and has a high friction; and is, therefore, difficult to handle without damaging the weak rope.

When the rope is removed from the impregnation bath for freezing, severe compression often occurs due to the weight of the wet foam rubber and the wet rope itself. One can say that this method preserves the primary structure of the rope as there is no collapse in the structure of the fibers themselves, however the secondary structure (i.e., the shape of the rope) suffers severely.



This method has been used for fairly well-preserved rope. The only method to conserve more deteriorated rope has until now been to use a high molecular weight PEG in high concentration. The results, however, have been aesthetically unpleasant as the ropes become stiff, dark, and flat.

### The new "Frankfurter Method"

The general procedure of the new method (called the "Frankfurter Method") involves five steps: cleaning, packing, freezing, freeze-drying, and impregnation.

Step 1. Cleaning with water to remove soiling. Tar should not be removed, as it is regarded as a part of the rope with the same historic value as the fibers. As any sort of bleaching will cause a weakening of the material and because the durability of a bleaching is questionable, it is generally omitted. Iron salts will, after the rope is packed, be washed out in a 0.1M solution of EDTA or 0.1–0.5M solution of acetic acid, both followed by washing in water. After this, the rope is repacked in clean packing materials.

Step 2. The rope is packed in a perforated polypropylene sheet which can be welded together. This package is fastened to a plate of perforated masonite for support. The whole package is placed in a plastic bag "Frankfurter," made in a size that fits the rope package perfectly. Before the last side is closed tightly, the bag is filled with water (See fig. 2).

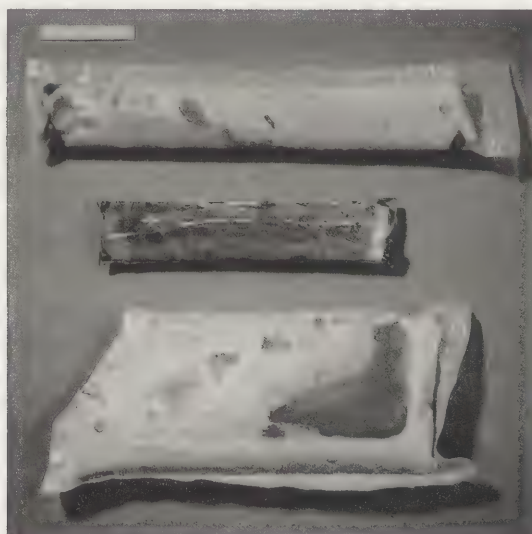


Figure 2. Frozen rope. The rope in the middle of the photograph is unpacked for freeze-drying.

Step 3. The rope is frozen at  $-27^{\circ}\text{C}$ .

Step 4. When the rope package is frozen the plastic bag is removed and the ice block "Frankfurter" is placed in the vacuum tank. One has to be very careful that the masonite plate is underneath the rope when the ice is sublimed. To ensure that the ice sublimates from the top, so that no ice lays on top of free rope material, the ice "Frankfurter" must be placed on an insulating material of approximately 3 cm thickness. The rope is freeze-dried at  $-20^{\circ}\text{C}$  and 50% RH (See fig. 3).

Step 5. When it is dry, the rope is unpacked. If necessary, a soft polyurethane (E2250) in ethylacetate can be applied with a hypodermic syringe (1). The rope is impregnated in at least 2 turns. One side has to harden before it can be turned upside down and impregnated from the other side.

### Evaluation of the "Frankfurter Method"

The polypropylene sheet is a light, transparent, and neutral material with stable dimensions and no friction that can be welded close to the perimeter of the rope, resulting in an optimum support. The packing is done very quickly. This,

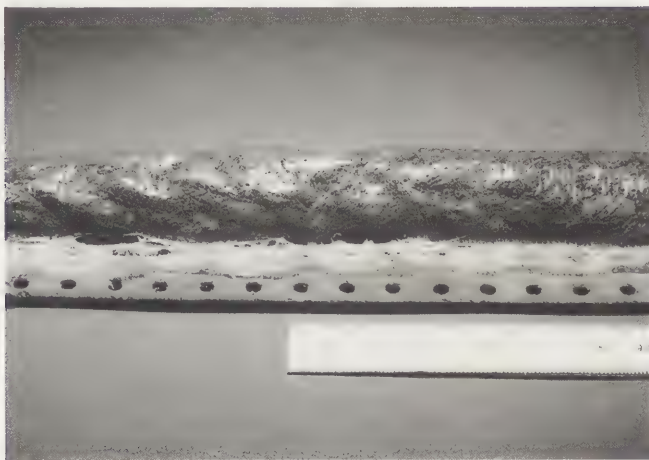


Figure 3. A freeze-dried rope still in the packing materials.

combined with freezing the rope floating freely in water, results in rope which, although deteriorated, has kept its original structure and shape. The tailor-made plastic bag makes the amount of water as small as possible, reducing the time for freeze-drying to a minimum.

Unfortunately, this improvement of the shape makes it more difficult to strengthen the rope because there is much more air in the structure than when using the traditional method where the fibers are more compressed. In spite of this, we have succeeded in making very weak rope quite stable and still flexible.

Because of the rapid evaporation in a fume cupboard, particularly when applying the polyurethane solution to certain types of nonabsorbant fibers, rapid evaporation of the volatile ethylacetate can result in polyurethane deposits on the surface, making the fibers shiny and preventing sufficient impregnation throughout the rope. Using a hypodermic syringe, the solution can be applied at the center, thereby penetrating the rope from the inside towards the surface and minimizing the risk of surplus polyurethane on the surface.

The traditional demand of reversibility to a conservation method is in this case not fulfilled, as the polyurethane cannot be removed later. Polyurethane is a rather stable material, although some aging tests—under extreme conditions not relevant to museum environments—result in decomposition (2).

The freeze-dried fibers are very light in colour and weight; they look rather dry. When impregnated, the rope appears darker, but it still has a brown rather natural colour.

Reversible methods for very deteriorated ropes are often not possible, as most methods do not stabilize the objects to a degree where loss of material can be avoided. Reversible methods can, however, be used for less deteriorated rope. These methods are based on impregnation with a water soluble bulking agent, which requires impregnation before drying. In these cases we cannot use the "Frankfurter" method because it would result in a surplus of impregnation material on the surface.

### The "Casing-Free Frankfurter Method"

For the less deteriorated objects, a modified method (called the "Casing-free Frankfurter Method") involves the following steps: cleaning, packing, impregnation, freezing in petroleum, and freeze-drying.

Steps 1 and 2. The same procedure as previously described.

Step 3. Depending on the degree of deterioration of the individual rope, it is impregnated with PEG 200–2000 or glycerol, 3–10% in water.

Step 4. The impregnated rope is transferred to a container with a non-polar organic petroleum solvent with a low freezing point, and is then cooled to  $-25^{\circ}\text{C}$ . The non-polar liquid is used to prevent the bulking agent from



diffusing out of the rope. Floating in the liquid, the rope will freeze and thereby be fixed in the swollen condition and the natural round shape.

Step 5. Controlled freeze-drying at  $-20^{\circ}\text{C}$  and 50% RH.

#### **Evaluation of the "Casing-free Frankfurter Method"**

The method allows a free choice of type and concentration of the water-soluble bulking material, giving optimum strength and flexibility. The freezing in a non-polar solvent results in a light colour, as no surplus impregnation material remains on the surface of the fibers. When possible to use, this method is preferable to the "Frankfurter" method due to its reversibility, the use of less toxic organic solvents, and the reuse of the petroleum solvent.

#### **Conclusion**

The two new methods described allow consolidation of ropes with polar as well as non-polar impregnation materials. The two methods both ensure fixation of the rope in the original shape.

The broad range of different treatments offered by these methods makes it possible to consider reversibility, strength, flexibility, colour, gloss, shape, future analysis, and other factors. Also, after treatment the ropes can be more safely exhibited, stored, or used as study objects.

#### **Supplies and materials**

Impregnation Agent E2250. Nederlandse Kunststoffen Chemie B.V., Emdenstraat, NL-7418 BR Deventer, Telephone 31-5700-28245, Telefax 31-5700-29359.

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## Abstract

A conservation method using sucrose and mannitol in the impregnation solution has been developed as a new, simple, and effective method for the preservation of multi-quality waterlogged wood. The sucrose-mannitol treatment makes it possible to conserve multi-quality wood in a one-step treatment. The method was tested for different Japanese waterlogged woods. The sugar concentration of the impregnation solution was increased gradually in four steps. First mannitol, then sucrose was added. The impregnation was done at 80°C. The method solved the problems of earlier mannitol treatments, such as whitening of the surface of the treated wood and insufficient consolidation. The sucrose-mannitol mixture gives the wood high stabilization. Anti-shrink efficiency values were generally over 90% for a wide range of wood quality; maximum water content was 226–668%.

## Keywords

Waterlogged wood, archaeological wood, conservation, sucrose, mannitol, sugar

## A Conservation Method for Waterlogged Wood Using a Sucrose-Mannitol Mixture

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## Introduction

Sugars as alternatives to polyethylene glycols (PEGs) are in increasing use for the conservation of waterlogged wooden remains in recent years. Some conservation groups successfully devoted themselves to the conservation of waterlogged wood with sugars, especially sucrose. In comparison with PEGs, sugar (sucrose) as a conservation material has a number of advantages, which are summarized in an earlier paper (1).

The idea to try a sucrose and mannitol mixture for the conservation of waterlogged wood came from two sources.

One was our experiences in sugar conservation and the other the advantages of the so-called two-step polyethylene glycol treatment for multi-quality timbers. We hoped that the two-step PEG treatment could be done in one step, in the case of sugars, using a mixture of two different sugar types.

Sucrose and mannitol seemed to be the most promising among the sugar types. Both of them have excellent dimension stabilization ability. Mannitol has smaller molecules and good diffusion characteristics, and penetrates very quickly into the wood structure. Therefore, it can be used favorably for less degraded wood. Mannitol has lower water solubility (15.7 wt% at 20°C) than sucrose. After the impregnation of the wood structure and as the temperature decreases, mannitol crystallizes before sucrose does. The situation is the same in the case of evaporation; if the sucrose-mannitol solution becomes increasingly concentrated as it dries, the mannitol crystallizes first, before the crystallization of sucrose begins. The mannitol crystals can stabilize the wood structure, acting as collapse protectors.

Sucrose has a higher molecular weight than mannitol. The penetration/diffusion ability is a little bit lower compared to mannitol. It forms large strong crystals. The water solubility is very high (67 wt% at 20°C). Therefore, it can become a good stabilizer for wood of middle and high deterioration, as it can bulk the void system of the wood.

It is well known that when mixing lower and higher molecular weight PEG in water in the two-step PEG treatment, the mixture will not solidify on drying; the result will be a sticky and greasy material. We tested this behaviour in the case of sucrose and mannitol mixtures. All mixtures crystallized well in the crystallization experiments. Therefore, the sucrose and mannitol mixture seemed to be promising for the conservation of multi-quality waterlogged wood in a one-step treatment. By using a sucrose and mannitol mixture in a one-step impregnation treatment, time and money can be saved.

## The two-step polyethylene glycol treatment

Archaeological wooden finds which contain various wood qualities cannot be stabilized satisfactorily in a traditional PEG treatment using only one grade of PEG. In an optimized two-step stabilization, two separate treatment baths are

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used, the first with low molecular weight PEG, and then a second with high molecular weight PEG. However, all wood qualities can be stabilized to a high degree if the right PEG concentrations of the treatment baths are chosen, that is, if the right amounts of PEG are incorporated into the wood structure (2, 3). The low molecular weight PEG (e.g., PEG 200) suits the stabilization of the slightly degraded wood parts and the high molecular weight PEG (e.g., PEG 3000) stabilizes the heavily degraded wood. Wood treated with mixtures of low and high molecular weight PEG remains sticky and greasy after drying. This consistency is characteristic for mixtures of pure PEGs, and is obviously transferred to the wood thus treated. So treatments with PEG mixtures can be regarded as not appropriate. The problem can be solved by the two-step treatment in which two different grades of PEG can be applied consecutively in two separate baths.

### Treatments using sugars

The conservation of waterlogged archaeological wood using sugars, according to our knowledge, was accomplished first by Italian researchers and published in the years 1970–1972 (4, 5). Since the 1970s, numerous research works and practical studies concerning sugar conservation were published (6).

In 1991 a conference was organized in Stade, Germany, in the conservation of archaeological wood using sugar. In the proceedings of the conference can be found the up-to-date conservation techniques and research directions (7). The sugar types used for conservation of waterlogged degraded wood are mainly sucrose; some publications describe the use of mannitol and sorbitol. The conservation techniques include heating of the sugar solution ("warm" conservation method) (8–11, 15), the hot-cold bath method (12), or the cheap impregnation method without heating ("cold" conservation method) (10, 13–16). The latter method is particularly suitable for larger wooden objects. It can, however, be used also for smaller ones.

Sugars can be used also in pre-treatments for waterlogged wood before freeze-drying (17–20). Sucrose gave the best result in appearance, followed by sorbitol and mannitol as a pre-treatment material (17).

There are several problems associated with the conventional mannitol method (18, 20): the surface of the treated wood is whitened with crystals of mannitol, fine cracks arise on the treated wood, and the waterlogged wood is not always consolidated sufficiently.

### Wood sample preparation—experimental impregnation

Four species of Japanese woods, mainly of medium and heavy degradation, were used for the study. The samples having the same water content were originally part of the same piece of wood.

The samples were prepared using an electrical circular saw. The cross cut surface varied between about 5–40 cm<sup>2</sup> and the thickness was generally 10 mm. The samples were as follows:

Japanese cypress ( <i>Chamaecyparis obtusa</i> )	
slightly degraded	$u_{\max} = 226\%$
moderately degraded	$u_{\max} = 307\%$
heavily degraded	$u_{\max} = 389\%$
Japanese red pine ( <i>Pinus densiflora</i> )	
heavily degraded	$u_{\max} = 399\%$
heavily degraded	$u_{\max} = 668\%$
Japanese chestnut ( <i>Castanea crenata</i> )	
heavily degraded	$u_{\max} = 509\%$
Sakaki ( <i>Cleyera japonica</i> )	
heavily degraded	$u_{\max} = 462\%$

### Maximum water content

For the determination of the maximal water content, the samples were submerged in distilled water in a container. The container was placed in a vacuum chamber and evacuated for at least 30 minutes. Then the vacuum was released for 30 minutes. This cycle was repeated two times. The samples were then weighed, oven dried at  $103 \pm 2^\circ\text{C}$ , and weighed again. The maximum water content ( $u_{\text{max}}$ ) was calculated as the percentage of the dry sample.

### Shrinkage measurement, calculation, and anti-shrink efficiency

Shrinkage measurements were made using steel pins as measurement stations. They were placed in tangential and radial anatomical directions in the cross grain surface of the wood sample. The dimensional changes were followed with calipers to within 0.005 cm.

Before taking the final shrinkage measurements, the wood was allowed to become dry and conditioned to the ambient climate for at least six months. It was then placed in a desiccator with a relative air humidity of 44% at  $20^\circ\text{C}$  for equilibration. The relative humidity (RH) in the desiccator was maintained by a saturated solution of potassium carbonate in water. The thickness of the samples in the longitudinal direction was 10 mm. Because longitudinal measurements were so small, they were ignored. Each sample was measured and weighed wet (before conservation and after conservation), then after air drying, and after equilibration.

The cross-section shrinkage ( $\beta_{\text{cs}}$ ) is calculated according to the equation:

$$\beta_{\text{cs}} = \beta_{\text{rad}} + \beta_{\text{tan}} - \beta_{\text{rad}}\beta_{\text{tan}}$$

The calculation of cross-section shrinkage makes it easier to transfer laboratory scale results to the behaviour of larger timbers in the conservation practise, as they only very seldom are cut according to the anatomical planes of the tree.

The dimension stabilization effect of a conservation treatment can be characterized by the anti-shrink efficiency (ASE).

The ASE is calculated as follows:

$$\text{ASE (\%)} = \frac{\text{Shrinkage (UW)} - \text{Shrinkage (TW)}}{\text{Shrinkage (UW)}} 100\%$$

where Shrinkage (UW) = shrinkage of untreated wood  
Shrinkage (TW) = shrinkage of treated wood

The shrinkage can be calculated as radial, tangential, longitudinal, or cross-sectional shrinkage ( $\beta_{\text{rad}}$ ,  $\beta_{\text{tan}}$ ,  $\beta_{\text{lon}}$ ,  $\beta_{\text{cs}}$ ); therefore, ASE can be related to the same directions ( $\text{ASE}_{\text{rad}}$ ,  $\text{ASE}_{\text{tan}}$ ,  $\text{ASE}_{\text{long}}$ ,  $\text{ASE}_{\text{cs}}$ ).

An ASE of 0% means that the wood has shrunk exactly as if it had been air-dried without any treatment; a negative value indicates that the wood has shrunk to a greater extent than without treatment. If the value is 100%, it means that the treatment has maintained the waterlogged, swollen dimensions perfectly. If the ASE is above 100%, then expansion beyond this state has occurred. The ASE is independent of the actual amount of shrinkage; this fact is very useful when comparing the efficiency of different treatments.

The ASE data are generally related to a relative air humidity. For instance, the value "ASE (50)" was calculated based on shrinkage of the air-dried wood at 50% RH. It is generally agreed that only if ASE values of more than 75% are achieved, can the method be accepted for stabilization of waterlogged wood (21).

### Treatment method

The wood samples were put into a 100 g/l mannitol solution in water in a covered plastic food box. The concentration of the solution is given in grams



of sugar per liter of water because the following additions of sugar change the total volume of the solution in the bath, but the original water amount in the bath does not change (if evaporation is prevented). The volume of the water incorporated in the waterlogged wood was ignored, because this was negligible compared to the water volume of the bath. The impregnation solution contained 0.1 wt% of the biocide Kathon CG; this concentration corresponds to 15 ppm active ingredients (isothiazolinones).

The bath was maintained at 80°C during the entire impregnation period. The sugar concentration was raised by 200 g/l mannitol after the first day, 300 g/l sucrose after the second day, and 450 g/l sucrose after the third day. After arriving at a sugar concentration of 1050 g sugar/liter, the wood samples remained in the solution for three more days. Table I outlines the schedule for the concentration increase.

Table 1. Schedule for the concentration increase of the bath using sucrose and mannitol in the impregnation solution at 80°C.

Time of day	Concentration increase (g/l water)	Total sugar concentration	
		g/l water	wt %
0	Start—Mannitol 100 g/l	100	9.1
1	100 g/l + Mannitol 200 g/l	300	23.1
2	300 g/l + Sucrose 300 g/l	600	37.5
3	600 g/l + Sucrose 450 g/l	1050	51.2
6	Removing the wood samples		

After the warm samples were removed from the solution, they were dipped and washed in warm water (80°C) for a few seconds to remove the superfluous sugar from the wood surface. Then they were air-dried.

### Results and conclusions

In Tables 2 and 3, the wood samples are arranged according to their species and degree of degradation (expressed as maximum water content  $u_{\max}$ ). Shrinkage characteristics and anti-shrink efficiencies are listed as they occurred on air-drying at 44% RH.

The sugar content of the samples is generally above 70% of the theoretical value; only the sakaki samples have taken up about 60% of the theoretical value. The sugar content of the samples increased proportionally to the degradation of the wood, which is due to the increase of the void volume in degraded wood. The average sugar uptake of the wood varied from 117.7% for Japanese cypress ( $u_{\max}$  226%) to 303.4% for Japanese red pine ( $u_{\max}$  399%).

The dimensional stabilization effect of the sucrose-mannitol treatment can be considered excellent in nearly every case. The ASE values are over 90%, except for the Japanese chestnut, which had average ASEs of 95.7% (radial), 84.1% (tangential), and 86.3% (cross section).

In one case, Japanese red pine ( $u_{\max}$  399%), the sugar solution has swollen the wood structure's negative shrinkage values, and ASE values greater than 100% resulted. According to our ongoing experiments on highly deteriorated wooden finds ( $u_{\max}$  over 600%), the final sugar concentration must be increased to 3400 g sugar/l water (77.3 wt%) to yield higher bulking. The colour of the conserved wood was natural.

Summarizing the results it can be said that the conservation method using sucrose and mannitol in the impregnation solution was effective and gave the wood high stabilization. This stabilization was characterized by anti-shrink efficiencies over 90% in a wide range of wood qualities ( $u_{\max}$  226–668%). The method solved the problems of the earlier mannitol treatments, namely the whitening of the surface of the treated wood, as well as the insufficient consolidation.

Table 2. The sugar up-take and the radial, tangential and cross section shrinkage and anti-shrink efficiencies of Japanese cypress, having different maximum water content ( $u_{max}$ ) after conservation using sucrose and mannitol mixture in the impregnation solution.

		Sugar incorporated		Shrinkage and anti-shrink efficiency					
		% of wood substance	% of theo- retical amount**	Radial		Tangential		Cross section	
No.				$\beta_r$ %	ASE <sub>r</sub> %	$\beta_t$ %	ASE <sub>t</sub> %	$\beta_{cs}$ %	ASE <sub>cs</sub> %
Japanese cypress u <sub>max</sub> = 226%	1.	113.7	81.9	0	100	0.21	93.9	0.21	95.9
	2.	113.4	81.7	0.13	92.3	0.28	91.9	0.41	91.9
	3.	126.0	90.8	0.17	90.4	0.16	95.3	0.33	93.5
Average		117.7	84.8	0.14	94.2	0.21	93.7	0.32*	93.8
Unconserved	4.	—	—	1.68	—	3.47	—	5.09	—
Japanese cypress u <sub>max</sub> = 307%	5.	110.7	58.7	0.20	95.2	0.40	95.3	0.60	95.1
	6.	179.1	95.0	0.20	95.2	0.31	96.4	0.51	95.9
	7.	178.5	94.6	0.30	92.9	0.30	96.5	0.60	95.1
Average		156.1	82.8	0.23	94.4	0.34	96.1	0.57*	95.4
Unconserved	8.	—	—	4.20	—	8.50	—	12.34	—
Japanese cypress u <sub>max</sub> = 389%	9.	173.7	72.7	0	100	0.35	96.8	0.35	97.5
	10.	180.3	75.4	0.43	87.6	0.30	97.2	0.73	94.8
	11.	170.4	71.3	0.36	89.6	0.45	95.9	1.16	91.7
Average		174.8	73.1	0.26	92.4	0.36	96.6	0.93*	94.7
Unconserved	12.	—	—	3.47	—	10.88	—	13.97	—

Shrinkages and ASEs are related to the air-dried condition RH = 44%.

\* Calculation was made by the help of the average  $\beta$  and  $\beta_r$ .

\*\* The theoretical amount is reached when all water in the wood has taken on the same sugar-concentration as the treatment bath. The theoretical sugar up-take was calculated:

$$\text{Theoretical sugar up-take \%} = \frac{c \rho u_{max}}{100} = 0.6144 u_{max}$$

where  $c$  = concentration of the sucrose-mannitol solution in wt % (51.2 wt %),  
 $\rho$  = density of the sucrose-mannitol solution  $\approx 1.2 \text{ g/cm}^3$ ,  
 $u_{max}$  = maximum water content of the treated wood.

The actual sugar up-take was calculated:

$$\text{Sugar up-take \%} = 3 \frac{\text{Mass of the wood sample after conservation, wet} - \text{mass of the wood sample before conservation in fully waterlogged condition}}{\text{calculated oven dry mass of the wood sample}} 100.$$
$$\text{Oven dry mass} = \frac{m}{\frac{u_{max}}{100} + 1}$$

where  $m$  = the initial mass of the wood.

But, volume occupied by sugar in the wood = (mass of sugar/density of sugar) = (mass of sugar/1.5) where density of the solid sucrose-mannitol sugar mixture  $\sim 1.5 \text{ g/cm}^3$ .

$$\begin{aligned} \text{Mass of expelled water} &= \text{volume of sugar} \times \text{density of water} \\ &= \frac{\text{mass of sugar incorporated}}{1.5} \end{aligned}$$

where density of water =  $1 \text{ g/cm}^3$ .

Mass change ( $\Delta m$ ) (after conservation, wet – before conservation, waterlogged):

$$\begin{aligned} \Delta m &= \text{mass of sugar incorporated in wood} - \text{mass of expelled water,} \\ \Delta m &= \text{mass of sugar incorporated} - \frac{\text{mass of sugar incorporated}}{1.5}. \end{aligned}$$

Mass of sugar incorporated =  $3 \Delta m$ .



Table 3. The sugar up-take and the radial, tangential and cross section shrinkage and anti-shrink efficiencies of Japanese red pine with two different maximum water contents ( $u_{\max}$ ), Japanese chestnut and sakaki, after conservation using sucrose and mannitol mixture in the impregnation solution.

	No.	Sugar incorporated		Shrinkage and anti-shrink efficiency					
		% of wood substance	% of theoretical amount**	Radial		Tangential		Cross section	
				$\beta_r$ %	ASE <sub>r</sub> %	$\beta_t$ %	ASE <sub>t</sub> %	$\beta_{cs}$ %	ASE <sub>cs</sub> %
Japanese red pine	13.	229.8	93.8	-0.77	116.4	-0.62	110.3	-1.38	113.2
$u_{\max} = 399\%$	14.	214.2	87.4	-0.41	108.7	-0.28	104.6	-0.69	106.6
	15.	240.9	98.3	-0.79	116.8	-1.13	118.8	-1.91	118.3
	16.	240.3	98.0	-0.73	115.5	0.02	99.7	-0.71	106.8
Average		231.3	94.4	-0.68	114.4	-0.50	108.4	-1.18*	111.2
Unconserved	17.	—	—	4.7	—	6.01	—	10.43	—
Japanese red pine	18.	310.2	75.6	0.30	91.5	0.31	95.1	0.61	93.7
$u_{\max} = 668\%$	19.	310.2	75.6	0.24	93.2	0.28	95.6	0.52	94.6
	20.	287.4	70.0	0.18	94.9	0.08	98.7	0.26	97.3
	21.	305.7	74.5	0.06	98.3	0.07	98.9	0.13	98.7
Average		303.4	73.4	0.20	94.5	0.19	97.1	0.39*	96.1
Unconserved	22.	—	—	3.55	—	6.30	—	9.63	—
Japanese chestnut	23.	246.0	78.7	1.93	94.5	2.09	95.7	3.98	94.0
$u_{\max} = 509\%$	24.	227.1	72.6	1.36	96.1	11.96	75.4	13.16	80.2
	25.	273.6	87.4	1.17	96.6	9.19	81.1	10.25	84.6
Average		248.9	79.6	1.49	95.7	7.74	84.1	8.81*	86.3
Unconserved	26.	—	—	34.9	—	48.70	—	66.6	—
Sakaki	27.	179.7	63.3	1.98	84.8	1.37	96.1	3.32	92.4
$u_{\max} = 462\%$	28.	165.3	58.2	0.85	93.5	2.86	91.9	3.69	91.5
	29.	162.0	57.1	0.52	96.0	3.25	90.7	3.75	91.4
Average		169.0	59.5	1.12	91.4	2.49	92.9	3.58*	91.8
Unconserved	30.	—	—	13.02	—	35.10	—	43.55	—

See footnotes on Table 2.

### Acknowledgements

This paper would not have been possible without the generous support of The Japan Foundation. The authors would like to express their deepest thanks to The Japan Foundation for offering and ensuring the support for the research work in Japan.

### Materials

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# Working Group 8

Photographic Records

Documents photographiques





## Résumé

Les autochromes, procédé de photographies en couleurs inventé par les frères Lumière vers 1903, sont communément considérés comme stables. Le but de cette étude est de déterminer les constituants les plus fragiles et d'établir s'ils ont subi une modification. Différents spécimens ont été analysés par spectrophotométrie et par Chromatographie Liquide à Haute Performance (CLHP). Ensuite, plusieurs des constituants des autochromes (colorants, vernis) ont été soumis à des vieillissements artificiels à la lumière et à la chaleur humide afin de mieux apprécier leur comportement pendant une conservation de longue durée. La dégradation d'un colorant particulièrement instable (vert de malachite orthochloré) a été étudiée. Les résultats de cette étude mettent en garde contre la fragilité de certains éléments constituants.

## Mots clés

Autochrome, procédé à réseau, analyse de colorants acides et basiques par CLHP, colorants du triphénylméthane, dégradation

Tableau A. Aspect visuel des réseaux étudiés.

Tons froids	Tons chauds
n°1: gris-vert	n°5: rose
n°2: bleu-rose	n°6: rose
n°3: gris-bleu	n°8: rose
n°4: vert	n°9: rose-orangé
n°7: gris-neutre	
n°10: vert	

## La plaque autochrome: analyses physiques et chimiques, étude de la stabilité des colorants

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## Introduction

Un autochrome est composé d'un mélange de féculles teintées en orangé, vert et violet, fixées sur une plaque de verre à l'aide d'un adhésif (premier vernis), protégées par un vernis (deuxième vernis) et recouvertes d'une émulsion panchromatique en noir et blanc. Si de nombreux articles ont été publiés sur les autochromes entre 1907, date de leur commercialisation, et 1935, époque à laquelle apparaissent les premiers films en couleur à développement chromogène qui annoncent la disparition des procédés à réseaux, très peu de renseignements d'ordre technique filtrent à l'époque des usines Lumière de Monplaisir à Lyon (France), dans un souci de protection industrielle [1]. Nous nous proposons d'analyser différents constituants et d'étudier leur stabilité.

## Analyse spectrophotométrique

Une dizaine de spécimens, sans grande valeur et de diverses provenances, a pu être collectée pour l'expérimentation. Sur ces plaques (numérotées de 1 à 10), nous avons éliminé la couche image pour ne garder que le support verre et le réseau trichrome.

## Etude macroscopique

En comparant visuellement les dix plaques, on note des différences appréciables, certains réseaux présentent une dominante chaude, légèrement rosée, pour d'autres la tonalité est plus froide, tirant sur le vert (tableau A).

Le spectrophotomètre a permis d'établir les coordonnées trichromatiques CIE-LAB (1976) des dix réseaux. Les écarts de couleur  $\Delta E^*$  entre ces réseaux pris deux à deux ont été calculés, la moyenne des valeurs obtenues est supérieure à 10. Malgré cet écart important, traduit en partie par une dispersion des points sur le graph CIELAB, il semble possible d'établir une filiation entre plusieurs réseaux. Si l'on considère un écart de couleur  $\Delta E^*=7,12$ , on peut constituer deux lots de réseaux dont les  $\Delta E^*$  entre les éléments pris deux à deux, restent en deçà de cette valeur limite. Le premier lot est formé des réseaux n°1, 2, 3, 7, et le second des n°5, 6, 8; quant aux réseaux 4, 9 et 10, ils n'ont pu être affiliés.

## Etude microscopique

Lorsque l'on observe les réseaux au microscope optique, on constate tout d'abord que la couleur des féculles varie en teinte et en intensité, d'une plaque à l'autre. C'est particulièrement vérifié pour les féculles violettes qui apparaissent bleues sur certains réseaux et tout à fait violettes sur d'autres. Les féculles vertes et orangées présentent, quant à elles, des disparités moindres selon les plaques. Il existe aussi des différences de structure géométrique. Certains réseaux contiennent des féculles sphériques bien séparées par du noir de carbone, et d'autres des féculles plus polyédriques et accolées.

Les coordonnées trichromatiques des féculles colorées de chacune des dix plaques ont été mesurées avec un microspectrophotomètre (Nanométriecs "docuspect 10"). Les points marquant la position des féculles violettes sont les plus dispersés, ce que confirme le calcul des écarts de couleur ( $\Delta E^*$ ). La moyenne pour les féculles violettes se situe aux alentours de 20 contre 12 et 10, respectivement pour les féculles vertes et orangées. Ces écarts de couleur sont le résultat des variations de chromaticité mais également de luminosité en particulier pour la

\* Auteur à qui la correspondance devrait être adressée.

Tableau B. Répartition du nombre de féculs colorés.

n°	% orangé	% vert	% violet
3	27%	36%	37%
7	28%	35%	37%
2	28%	38%	34%
6	30%	39%	31%
9	31%	35%	34%
5	31%	36%	33%
1	31%	36%	33%
10	31%	37%	32%
8	32%	36%	32%
4	33%	33%	34%

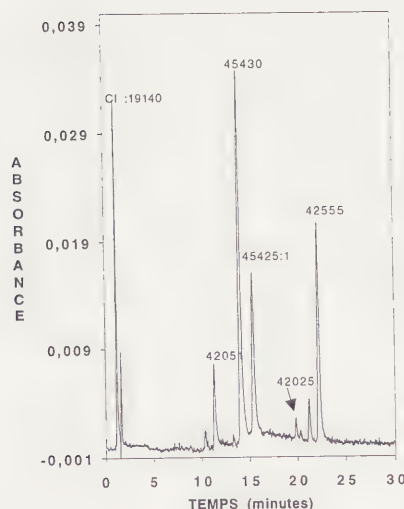


Figure 1: Analyse par HPLC d'une plaque autochrome—Détection à 530nm

- Colonne **chromspher B** (Chrompack, n° de catalogue 28224), diamètre 3,0mm, longueur 10cm.
- débit: 0,4 ml/min.
- température: 40°C
- éluant A: solution aqueuse à 0,01M de perchlorate de sodium ajustée à pH 4,5 avec de l'acide perchlorique.
- éluant B: solution à 0,01M de perchlorate de sodium dans l'acétronile.
- gradient: gradient linéaire

temps (min.)	%A	%B
0	90	10
15	25	75
25	0	100
30	0	100

fécule violette où la différence de densité entre le réseau 5 et le 4, par exemple, s'élève à plus de 0,7. Les différences de couleurs des féculs peuvent donc justifier à elles seules les variations de colorations observées à l'oeil nu entre nos dix échantillons.

L'observation de ces réseaux au microscope montre que les réseaux à fécule bleue correspondent aux plaques à ton froid et ceux à fécule violette, aux plaques à ton chaud.

### Etude du nombre de féculs teintés

Des plages, d'un dixième de mm<sup>2</sup>, sont enregistrées à l'aide d'une caméra vidéo CCD et traitées numériquement. Pour déterminer la quantité de chaque lot de fécule, il suffit d'éclairer le réseau sur le microscope avec une lumière respectivement violette, verte et orangée au moyen de filtres. Dans le premier des cas, seules les féculs violettes sont activées (transparentes). Les féculs accolées sont séparées par un traitement morphologique propre et on dénombre ainsi la proportion de féculs violettes. L'opération est répétée, sur la même plage, pour les deux autres couleurs. Sur chaque plaque autochrome dix plages sont ainsi analysées et la moyenne des grains de chacune des couleurs est établie (voir tableau B).

Ces valeurs confirment que les féculs orangées sont minoritaires et que les féculs vertes, contrairement à ce qui est décrit dans la littérature, ne sont pas toujours les plus nombreuses.

### Discussion

Ces analyses microscopiques et macroscopiques mettent en évidence quantitativement et qualitativement les différences entre les réseaux colorés. Certaines d'entre elles sont incontestablement liées à une hétérogénéité de fabrication, c'est le cas des fluctuations du nombre de féculs orangées, vertes et violettes selon les plaques. L'origine des différences de couleurs des grains de fécule ou des réseaux, n'a pu être déterminée avec précision. Les irrégularités de fabrication y prennent sans doute une part importante, on peut néanmoins suspecter la dégradation de certains colorants, en particulier dans les féculs violettes. Sur les plaques examinées, nous avons remarqué que les réseaux à ton froids contiennent des féculs bleues et ceux à tons chauds, des féculs violettes.

### Analyse des colorants des plaques autochromes par CLHP

L'analyse en chromatographie liquide à polarité de phase inversée [2] a permis d'identifier la plupart des colorants présents dans les réseaux (voir Fig. 1 et tableau C).

Tableau C. Colorants identifiés dans des réseaux autochromes.

n° de C.I.	Noms usuels	Fécule
—	vert de malachite m-chloré	violette
19140	tartrazine	orangée, verte
42025	vert de malachite orthochloré	violette
42051	bleu patenté	verte
42555	violet cristallisé	violette
45425:1	diiodofluorescéine	orangée
45430	érythrosine	orangée
45440	rose bengale	orangée

### Discussion

L'analyse d'une dizaine de réseaux autochromes confirme l'origine des colorants utilisés dans la fabrication. Ce sont des composés acides ou basiques, de la famille des triphénylméthanes, des xanthènes, ou monoazoïques tels qu'ils ont été décrits dans la littérature ou les archives. D'autres composés ont été mis en évidence: des impuretés comme la diiodofluorescéine (impureté de l'érythrosine) ou le vert de malachite métachloré, sans doute présentes dans les colorants commerciaux





l'apparition d'un réseau de craquelures. Ce phénomène déjà rapporté par Peter Krause [4] sur des autochromes anciens irradiés, peut donc être attribué avec certitude à la présence du second vernis et sera étudié ultérieurement.

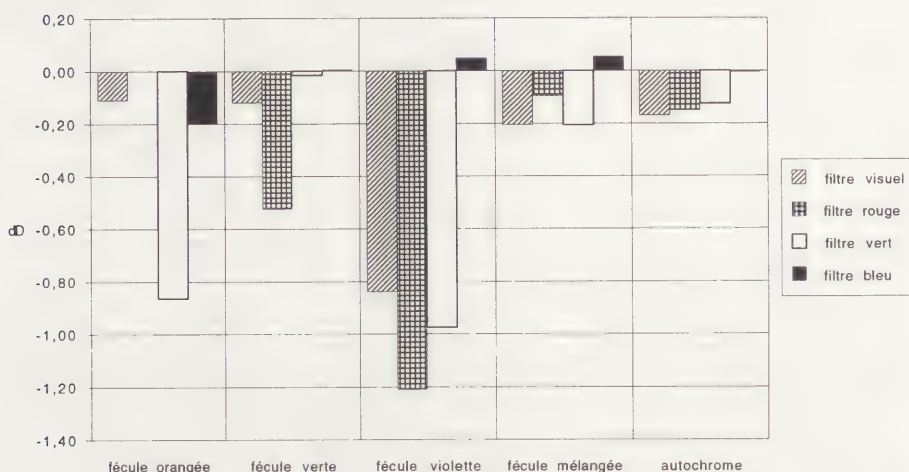


Figure 3: Comparaison des pertes de densité mesurées sur les trois fécules puis sur le mélange après une exposition à la lumière: 25 kJ/cm<sup>2</sup>, 30°C, 50% H.R.

Comme on peut le constater (voir Fig.3), les pertes de densité mesurées sur le mélange de fécules (violette, orangée, verte) sont moins importantes que celles mesurées sur chaque lot. Ainsi, après avoir reçu une énergie de 25kJ, les fécules bleues ont perdu 1,20 de densité rouge alors que le mélange n'a varié que de 0,10! Une tentative d'explication peut être donnée en considérant la spécificité du procédé; contrairement aux procédés modernes soustractifs où la dégradation des trois couleurs réunies aurait été la somme des altérations de chacune des couleurs, dans un procédé additif il ne faut plus additionner mais moyenner les pertes de densité, car les couleurs ne sont plus superposées mais juxtaposées. Ainsi les fécules violettes ne représentant qu'un pourcentage du mélange (moins d'un tiers), leur dégradation n'est prise en compte que dans la même proportion.

$$\Delta D(\text{réseau}) = \alpha \Delta D(\text{fécules violettes}) + \beta \Delta D(\text{fécules vertes}) + \gamma \Delta D(\text{fécules orangées})$$

$\alpha, \beta, \gamma$ : proportion de fécules violettes, vertes, orangées ( $\alpha + \beta + \gamma = 1$ )  
 $\Delta D$  perte de densité

Ceci est schématisé dans la figure 4. (voir Fig. 4)

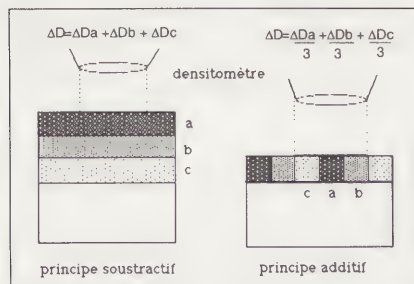


Figure 4: Représentation schématique de la mesure de la densité sur un procédé de type soustractif et un procédé de type additif.

Si l'utilisation d'un densitomètre conventionnel sur une plaque autochrome permet de mettre en évidence des variations de densité, il est difficile d'estimer ce qu'elles traduisent à l'échelle du réseau, les décolorations de certaines fécules peuvent être en effet très prononcées.

### Stabilité des colorants dans l'obscurité

La plupart des autochromes étant conservés à l'abri de la lumière, nous avons voulu déterminer si, dans des conditions normalisées de conservation, certains colorants sont susceptibles de se dégrader. Comme pour les vieillissements à la lumière, nous avons teinté des feuilles de papier Whatman avec les différents colorants et nous les avons soumises à un vieillissement à 90°C, 60% H.R. Les échantillons ont été mesurés régulièrement à l'aide d'un densitomètre.

### Résultats et discussions

Parmi les colorants étudiés, le vert de malachite orthochloré apparaît encore le plus fragile, le violet cristallisé semble quant à lui, étonnamment plus stable (voir Fig. 5). Après une centaine d'heures sa décoloration paraît se stabiliser, c'est le cas aussi du bleu patenté. L'ordre de stabilité relative dans l'obscurité est le suivant:

peu stables: vert de malachite métachloré, vert de malachite orthochloré, diiodofluorescéine, érythrosine

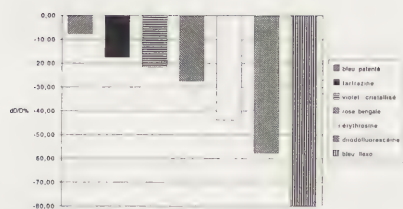


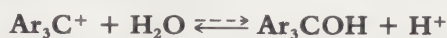
Figure 5: Stabilité relative dans l'obscurité de différents colorants imprégnés sur du papier Whatman, après 664 heures (90°C, 60% H.R.).



moyennement stable: rose bengale

stables: bleu patenté, tartrazine, violet cristallisé.

On peut donc prévoir qu'au cours du temps les fécules bleu-violet deviendront plus violettes, les fécules orangées plus jaunes; quant aux fécules vertes, elles resteront pratiquement inchangées. D'une façon globale, la couleur du réseau vire vers une tonalité plus chaude. Il nous a paru important d'évaluer si la décoloration dans l'obscurité du vert de malachite orthochloré, à température ambiante, pouvait s'apprécier au terme de quelques années ou de plusieurs décennies. La dégradation du colorant passe par la formation du carbinol, le colorant est en équilibre avec le triphénylcarbinol. Les premiers stades de cette réaction, en milieu aqueux, suivent une cinétique du premier ordre, ou du second ordre en présence d'ions hydroxydes [5,6]:



Nous avons placé du papier imprégné de vert de malachite orthochloré et de la fécule teintée et vernie à différentes températures allant de 50 à 90°C (60% HR). Les droites d'Arrhénius ont permis d'extrapoler à 21°C (tableau D). L'énergie d'activation de la réaction est de 72 kJ/mole.

Tableau D. Extrapolation de la durée de vie du vert de malachite orthochloré.

	Temps pour atteindre 20% de perte de DO à 21°C	Temps pour atteindre 40% de perte de DO à 21°C
Colorant sur du papier	342 jours	2,4 années
Colorant sur de la fécule	3,7 années	—

La dégradation du colorant adsorbé sur de la fécule est plus lente que lorsque celui-ci est imprégné sur du papier. Bien que cela représente une durée quatre fois supérieure à celle du colorant sur papier, le résultat n'est guère rassurant. Néanmoins, la plaque autochrome a quelques atouts supplémentaires que nous n'avons pas pris en considération et qui accroissent la longévité du colorant en limitant la diffusion de l'eau et de l'oxygène. Ce sont:

- la lamination des grains
- la couche de gélatine
- le vernis de protection appliqué par le photographe
- le verre de doublage.

### Stabilité à la lumière du deuxième vernis

Lors de nos expériences de vieillissement à la lumière, nous avons observé que le second vernis (à base de gomme dammar, de nitrate de cellulose et d'huile de ricin) est à l'origine de la formation de craquelures sur le réseau. Les trois vernis suivants sont préparés:

- verniss (1): gomme dammar dans l'acétate d'éthyle
- verniss (2): gomme dammar et huile de ricin dans l'acétate d'éthyle
- verniss (3): gomme dammar et nitrate de cellulose dans l'acétate d'éthyle

Ces vernis sont ensuite appliqués sur des plaques autochromes où nous avons substitué la couche de fécule par une couche de noir de carbone, permettant ainsi de visualiser immédiatement l'apparition des craquelures. Ces échantillons ont été exposés à la lumière (50% H.R., 30°C).

### Résultats et discussion

Sur la plaque recouverte du vernis (2) on n'observe pas d'altérations, avec le vernis (1) on note quelques fines craquelures mais très limitées, tandis qu'avec le vernis (3) les plaques révèlent un réseau de larges craquelures identique à celui décrit antérieurement. Le nitrate de cellulose est donc le constituant du vernis responsable de l'altération. Ces craquelures se propagent de façon importante dans la partie non exposée, même lorsque l'exposition est arrêtée. L'analyse par spectroscopie infra-rouge et des travaux antécédents [7] montrent que ce réseau de craquelures est dû à la réticulation à la lumière du nitrate de cellulose. Celle-

ci génère des tensions qui sont transmises au premier vernis, son adhérence au verre n'est pas assez forte, des craquelures apparaissent.

### Conclusion

L'analyse approfondie d'autochromes anciens a révélé qu'il existait d'une plaque à l'autre de grandes différences colorimétriques dues à la fabrication (formulation des bains de teinture, proportion de féculles teintées). Cependant une dégradation du réseau (décoloration, migration de colorants) a été mise en évidence sur plusieurs des réseaux étudiés. Les analyses chromatographiques sur une dizaine de plaques ont montré peu de différences dans la composition tinctoriale. Malheureusement, la plupart des colorants sont fugitifs à la lumière et, au cours d'une exposition prolongée, le réseau autochrome vire vers des tonalités chaudes. Même lorsqu'ils sont conservés à l'abri de la lumière, certains de ces colorants se dégradent. Ainsi, il est probable que, dans des conditions de conservation non contrôlées, le vert de malachite orthochloré se soit déjà en partie dégradé. Les féculles bleu-violet acquièrent une tonalité violette plus marquée. Nous n'avons pu déterminer si ce phénomène est à l'origine des écarts de coloration que l'on peut constater aujourd'hui sur ces féculles selon les plaques. Toutefois à la vue des résultats de cette étude on peut le suspecter légitimement. Le second vernis contient du nitrate de cellulose qui se détériore et jaunit au cours d'une irradiation. Dans des cas extrêmes, un réseau de craquelures se développe. Cette altération initiée à la lumière peut se propager dans l'obscurité. Les conditions hygrométriques jouent un rôle important, un excès d'humidité accélère la dégradation du nitrate de cellulose et celle des colorants, il induit la migration de ces derniers dans le réseau. La conservation des plaques autochromes doit donc se plier aux exigences particulières du procédé. Le choix de l'humidité à recommander pour l'archivage doit prendre en compte la structure multicouche de la plaque. Une humidité relative trop basse produit des tensions dans la couche de gélatine et peut favoriser le décollement de la couche image, voire de l'image et du réseau. Plus que dans tout autre procédé, l'excès d'humidité a des effets néfastes. De même une température de stockage limitée à 21°C est impérative, et inférieure à 18°C recommandée.

### Remerciements

Cette étude a pu se faire grâce à l'aide du Musée Albert Kahn (Boulogne, France), et de la Mission du Patrimoine Photographique. De nombreuses personnes et sociétés ont prêté leur concours en particulier Madame Chantal Garnier, Madame Pascale Richardin, Monsieur Paul Génard, Monsieur Trarieux, Monsieur Jean Demure, Monsieur Jean Seyewetz, Madame Chemin-Doublier, Madame Sonia Bôve, Monsieur Chardère et ses collaborateurs de l'Institut Lumière, les sociétés BASF, Degussa, ICI (Monsieur Dupont), Kodak-Pathé (Monsieur Gaurat), Lejeune-Safic Alcan, SNPE, Steiner.

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Abstract

The stability of four types of colour transparencies is discussed, for storage at room temperature, storage at elevated temperature and relative humidity (RH), and for accelerated light ageing. When complicating factors such as heat and RH sensitivity and colour recovery in the dark are taken into account, the films can be ranked: Kodachrome, then Fujichrome, have the best dark stability, while Fujichrome and Ektachrome have the best stability to light. Agfachrome showed loss of colour after eight years in the dark. Underexposed and slow films last longer, and RH affects storage stability more than temperature. All the films have a lightfastness worse than ISO Blue Wool Standard 4, unless protected by an ultraviolet filter.

Keywords

Colour transparencies, colour slides, fading, storage stability, dark stability

Colour Transparencies: Studies on Light Fading and Storage Stability

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Introduction

Transparencies are used in conservation records, and are expected to survive for decades at room temperature, generally not in a carefully-controlled environment. The more interesting slides illustrating a treatment may be projected regularly as well. For continuously-running audiovisual presentations it is accepted practice to show duplicate sets, while storing a master set. This paper describes the color changes found in eight-year-old 35mm slides, stored in fairly typical conditions. Results on short-term storage at elevated temperature and/or relative humidity are discussed, with their implications for the life expectancy of the films. Accelerated light ageing of the same films was reported by the authors in 1987 (1); these results are summarised and augmented. The authors are not aware of other studies on the storage stability or lightfastness of slides, subsequent to those reviewed in 1987, though the dark stability and expected lifetime of cinematographic film have been studied since then (2).

The interpretation of results from accelerated ageing is discussed. Exposure to light is expressed as the accumulated dose in megalux-hours: this study is also relevant to the display of light-sensitive materials. Large-format transparencies are used in social history and natural history exhibitions, where original or duplicate material may be displayed. There are also occasions when the transparency is itself an object to be conserved.

Film types selected for study and their examination

In 1982, films manufactured by Kodak (Ektachrome and Kodachrome), Fuji and Agfa were purchased, in the full range of film speeds then available (see table 1). For Ektachrome films, professional and non-professional films of the same

Table 1. Film types selected for study. Speeds of 100ASA or less are regarded as "slow".

Film	Code	Speed (ASA)	Type	Lighting
Ektachrome	EL	400	non-professional	daylight
Ektachrome	ED	200	non-professional	daylight
Ektachrome	EPD	200	professional	daylight
Ektachrome	ET	160	non-professional	tungsten
Ektachrome	EPT	160	professional	tungsten
Ektachrome	ER	64	non-professional	daylight
Ektachrome	EPR	64	professional	daylight
Ektachrome	EPY	50	professional	tungsten
Kodachrome	KR	64	non-professional	daylight
Kodachrome	KM	25	non-professional	daylight
Fujichrome	RH	400	non-professional	daylight
Fujichrome	RD	100	non-professional	daylight
Agfachrome	CT21	100	non-professional	daylight
Agfachrome	CT18	50	non-professional	daylight

\* Author to whom correspondence should be addressed.

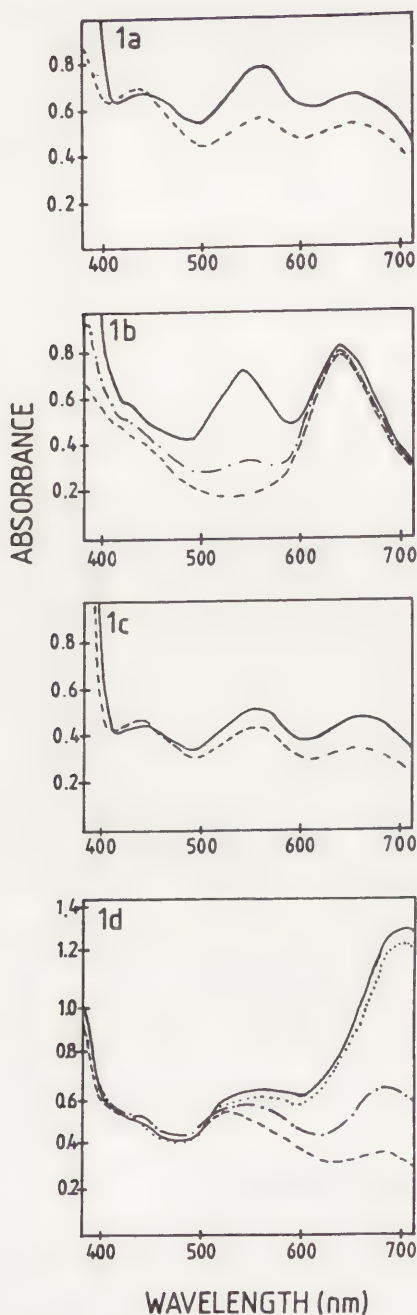


Fig. 1. Absorbance spectra for typical normally-exposed films, where the subject was a Kodak Neutral Test Card. a. Ektachrome ET 160ASA b. Kodachrome KR 64ASA c. Fujichrome RH 100ASA d. Agfachrome CT21 100ASA. 1d shows, from top to bottom, newly-processed film, film after 50 and 100 hours accelerated light ageing, and film from 4 years dark storage.

Table 2. Wavelengths of absorbance peaks (in nanometres).

Film	Yellow	Magenta	Cyan
Ektachrome	437	563	657
Kodachrome	430	543	640
Fujichrome	440	550	655
Agfachrome	437	560	700

speeds were obtained, for both daylight and tungsten light. All other film types available then were daylight and non-professional. All were used soon after purchase, a good practice for professional films with short shelf-lives but not necessarily so for non-professional films. One film of each type was exposed and processed in the usual manner, i.e. by the manufacturer for Fujichrome, Agfachrome and Kodachrome films and by a commercial processor for the Ektachrome films.

It had been anticipated that there would be differences in stability to light for different film speeds and for professional/non-professional films. In fact there was little change in behaviour with respect to these variables. Dye formulations are not changed very frequently (3), and these materials were sold for a number of years and may still be sold unchanged. Kodachrome professional film continues to employ the same emulsion (4). No attempt was made to examine currently-sold films.

The "subject" was the grey side of a Kodak Neutral Test Card, evenly illuminated with daylight or tungsten photographic lights as appropriate. Some additional shots were taken at one stop over- and under-exposed.

The absorbance from 380nm to 720nm was measured with a Perkin-Elmer 550S UV/visible spectrophotometer with an integrating sphere. After background correction, the height of a well-defined peak can be measured to  $\pm 0.01$  absorbance units. Changes in absorbance greater than "just detectable" were processed by a customised software package and restated in the form of CIELAB 1976 colour differences in terms of a 2° observer, and CIE source A, tungsten light. This light source is appropriate because projectors use tungsten-halogen bulbs of similar colour temperature. The absorbance spectrum of each transparency has three peaks at different wavelengths (see table 2), corresponding to the yellow, magenta and cyan colour couplers (see figs. 1a-d). It appears that each manufacturer uses similar dye chemistry for films of all speeds. (Film speed is controlled by the size and shape of the dye grains (5). The chemistry of colour transparencies has been described in the scientific literature (6), but is not needed here.) Quoting large colour changes as changes in absorbance of the yellow, magenta and cyan peaks is misleading, since one is comparing measurements at different wavelengths. The eye is less sensitive to the extremes of the visible spectrum (7), for example, to the cyan peak of Agfachrome film at 700 nm.

### Ageing conditions

#### Dark storage

Films were stored in non-archival slide hanging files or polythene folders, undisturbed in filing drawers in non-air-conditioned offices, and later in an office air-conditioned to 50% RH and 18–20°C. The RH was likely to have been higher than that recommended for museum storage conditions, since air in rarely-opened drawers tends to be cooler and more damp than in the room. Most conservation files are kept in similar conditions.

#### Elevated temperature and relative humidity

Storage tests were carried out as a student project on the same batch of films (8). Film samples were suspended in stoppered test-tubes containing salt solutions to provide fixed RHs of 60% or 75%, and were stored in an oven at 20, 40, or 60°C for 60 days.

#### Accelerated light ageing

Normally-exposed samples of all film types, and other over- and under-exposed samples, were placed in the sample cells of a Microscal Lightfastness Tester with a high-pressure mercury tungsten bulb (Philips 500W MBTL) cooled with a fan. The RH was 59–65%, and the temperature of the grey films was between 30°C and 56°C (the latter recorded by a "black panel" thermometer). All films were exposed from the emulsion side, as in slide projectors. They were exposed for 100 hours to a dose of 3.5 megalux-hours, which causes perceptible fading in ISO Blue Wool Standard 4. Most accelerated ageing is for 600–1000 hours. In fact, the Microscal illuminance of approximately 35,000 lux is benign com-



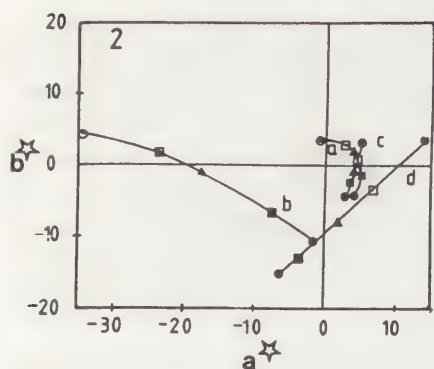


Fig. 2. Chromaticity coordinates of the films from Fig. 1, before ageing (solid circle), and after 10, 30, 50 and 100 hours of accelerated light ageing.

pared to the exposure to C.500,000 lux and about 80°C (9,10) in most projectors. A slide projected for an hour (as a useful one might be, over a lecture course) receives a dose of 0.5 megalux-hour, the same dose accumulated by an artwork exposed to 50 lux for 6–7 years during museum opening hours.

#### *Extensions of accelerated light ageing studies*

Representative samples were exposed with and without an ultraviolet filter (Encapsulite C10, whose transmittance has been published (11)), with lengthened exposure times to compensate for the ~90% transmittance of the filter, and illuminated from base or emulsion sides.

## Results and discussion

### *Dark storage*

Colour changes in dark storage are just significant after 8 years. They are shown in Table 3, first as an overall colour difference  $\Delta E$  after four and eight years

Table 3. Colour changes arising from dark storage, by film type. The greatest changes shown by any film from a given manufacturer are presented. Negative changes indicate a loss of colour. First and second columns: CIELAB colour differences. Later columns: changes in absorbance in each colour coupler.

Film	$\Delta E$		Yellow	Magenta	Cyan
	4 years	8 years			
Ektachrome	1.7	>2	+0.01–0.03	–0.02–0.06	–0.01–0.02
Kodachrome	1.3	>2	–0.04–0.05	–0.02–0.04	–0.01–0.04
Fujichrome	0.51	~1	–0.01–0.03	–0.01–0.03	–0.01–0.02
Agfachrome	0.48	≥2	–0.01–0.19	–0.01–0.09	–0.04–0.48

storage, then as the change in absorbance for each colour coupler after eight years storage. Where several films of the same type, namely Ektachrome, could be compared, the results are aggregated. After 8 years, Ektachrome films showed a slight shift in colour balance, becoming more yellow, while losing magenta and cyan. This is not unreasonable chemically, since most degradation products will be yellow. The others maintained their colour balance, while growing paler. The colour change in the Agfachrome film (see fig. 1d) is comparable to that induced in the “best” film by 100 hours of accelerated light ageing (see below). It is doubtful whether a viewer could recall a change from the appearance of eight years earlier: the films’ useful lifetime is not yet run.

### *Storage at elevated temperature and RH*

Interpretation of colour changes in films exposed to high RH is more problematic. The film absorbs water, the base swells on the unconstrained side and the dye layers are squeezed together: there is an apparent increase in absorbance. Similarly, a film at elevated temperature and normal RH loses water, shrinks, and also appears to have an increased absorbance. This notwithstanding, colour loss was greater at temperatures of 60°C and 80°C than at 20°C, and greater at 75% RH than at 60%, for the same storage times. Others (8,12) have used changes in absorbance to estimate the time for a 10% change in absorbance for the most fugitive colour coupler, when the films are stored at room temperature (Table 4). Again, one cannot interpret their results as suggesting an equal change

Table 4. Estimated lifetime for a 10% loss of absorbance in the most fugitive colour coupler for each film, at 24°C and 40% RH.

Film	Time	Colour coupler	Reference
Ektachrome	20 years	yellow	8, 12
Kodachrome	90 years	cyan	12
Fujichrome	>50 years	yellow	8
Agfachrome	20 years	cyan	

in colour after these periods, because two separate colour couplers, and different wavelengths, are involved. The results for Fujichrome and Ektachrome are directly comparable, because their colour couplers have the same peak wavelengths. Fujichrome certainly has a much better life expectancy. Kodachrome undoubtedly has a good life expectancy and its manufacturers have always claimed that it has markedly better dark stability than Ektachrome (13). Work on a range of cinematographic films (5) also showed that Kodachrome had the best dark stability. But Agfachrome film could be judged too harshly from Table 4 alone, since the wavelength at which this colour change takes place is distinct from the other films, and one where the eye cannot discriminate colours well.

Colour loss was negligible at 40°C and 60% RH for 100 hours for Kodachrome, Agfachrome and Fujichrome films, but not for Ektachrome. This indicates that some of the colour loss during accelerated ageing was due to the above-ambient temperature for Ektachrome films, but not for the others, so they may have been judged too harshly.

#### *Accelerated light ageing—previous results*

Only a few results are presented here (see Table 5 and fig. 2). Fig. 2 also illustrates differences in colour rendering among the films: the grey "subject" plots very

Table 5. Colour differences in normally-exposed films of various speeds. Results by other workers (10) for 0.8 megalux-hours are included for comparison.

Film	Speed (ASA)	$\Delta E$ 0.8	After light exposure (Mlux-hr)		Remarks
			1.5	3.0	
Ekta ED	200	3.5	8.3	16	yellowier
Ekta EPD	200		8.2	15	yellowier
Ekta EPT	160	5.2	6.0	12	yellowier
Ekta EPR	64		6.9	14	yellowier
Koda KR	64	10	29	41	greener
Fuji RH	100	2.8	5.3	9.7	yellowier
Agfa CT21	100		18	29	redder

close to zero, and if the films had perfect colour rendering, their chromaticity coordinates would overlie it. Ektachrome and Fujichrome lie closest. The other two film types look more blue-green than the "subject". There was no significant difference on ageing between professional/non-professional and daylight/tungsten films. Colour differences were slightly less in slower films than in fast ones. Underexposed films had slightly smaller colour differences, and overexposed films slightly greater ones, in all cases. These "slight" variations would amount to less than a factor of two. The greatest distinction in colour changes lies in film type: Fujichrome films showed the smallest changes, followed by Ektachrome, Agfachrome and Kodachrome. Loss of colour in Kodachrome is due to the complete destruction of the magenta colour coupler, hence its greenness. Further ageing could not do any more harm in this respect. In fact, there was no recovery of colour in any of these films after 2000 hours, or twenty times the exposure period, in contrast to earlier studies on different films (4).

In the context of acceptability for conservation documentation, Fujichrome would "pass" after 50 hours ageing, and perhaps after 100 hours, while the other colour changes give cause for concern. Assuming reciprocity, Fujichrome transparencies could "withstand" 10–20 years of exposure to 50 lux without noticeable loss of colour, Ektachrome perhaps 10 years, and the other film types less. In an illuminated display, they are more likely to be exposed to 500–1,000 lux, which suggests that one year at best is their useful lifespan. Neither 35mm slides nor large-format transparencies are marketed as archivally stable products, or long-life display materials. It was assumed above that a CIELAB colour difference of 5–10, easily noticeable when one compares "before and after" material, is acceptable when no "before" material is available for comparison.



Otherwise, a colour difference of 1.0 is just noticeable and can be measured, while a colour difference of 1–2 between two adjacent samples can be seen in good lighting. This is easier to put into context than the 10% change in absorbance, so convenient in chemical terms, used by other workers (8,12).

#### *Accelerated light ageing—new results*

It is to be expected that the same exposure from the emulsion and base sides of the film will produce different colour changes. Colour transparencies consist of a base, cyan image, magenta image, an ultraviolet absorber and a yellow image, not always in that order. Light is filtered by each layer, so succeeding layers “see” selected colours only, and some avoid ultraviolet exposure, depending on the direction of the incoming light. It can be seen from Table 6 that Fujichrome

Table 6. Colour changes in normally-exposed films, for 3 megalux-hours accelerated ageing in various conditions: emulsion/base exposure with and without ultraviolet filter.

Film	Speed (ASA)	Emulsion no filter	Base no filter	Emulsion UV filter	Base UV filter
Ektachrome ET	160	16	13	8.1	7.5
Kodachrome KR	64	41	48	24	26
Fujichrome RH	100	9.7	4.4	3.2	3.7
Agfachrome CT21	100	29	13	3.7	2.8

and Agfachrome films lose colour to very different degrees, depending on the direction of exposure, and that exposure through the base (such as back projection and display on a light-box) is preferable for them. There is less difference for Ektachrome and Kodachrome: the latter loses more colour if exposed through the base.

A UV filter between the film and light source influences the colour change, dramatically so in the case of Agfachrome film. Its useful display lifetime could be increased several times by the presence of a UV filter. In fact, changes to current films could well be due to the presence of improved or longer-life internal UV absorbers.

#### **Implications for the storage and display of transparencies**

The recommendation is usually made that photographic material should be stored at low temperatures: storage recommendations over the years have been summarized recently (15). Very few conservation records are refrigerated however, and the condensation which might form each time the records were consulted at room temperature could be as damaging in the long term as room temperature storage. A good compromise would be to store transparencies in a heated room (c.18°C) to avoid the higher RH found in colder rooms, since RH has a greater effect on dark stability than temperature. “Ideal” museum conditions of 50% RH would be suitable. Silica gel used as a drier or buffer would have it uses, though the manufacturers themselves (13) never recommend an RH lower than 30%.

The low-grade storage envelopes used in this study had a noticeable effect after 8 years of storage. Microscopic spots of (presumably) migrating plasticiser had been deposited on all the slides. Achromatically stable ones are obviously preferable for both 35mm slides and large-format transparencies, and some research has been carried out on such materials (16). Plasticiser from the film base had also been implicated in film deterioration (17)—this cannot be eliminated as a contribution to deterioration.

This study has confirmed that Kodachrome film (purchased in 1982) is indeed among the best for dark stability, and has also shown that Fujichrome films are stable, and might even be comparable to Kodachrome. Cibachrome films, not studied here, are also said to have excellent dark stability (18,19), possibly surpassing that of Kodachrome. Ektachrome and Agfachrome films would show significant loss of colour over a working lifetime and indeed Agfachrome changed colour measurably over 8 years.

Kodachrome, however, was the worst when subjected to accelerated light ageing, and Fujichrome and Ektachrome were the best. Assuming reciprocity holds, three hours projection would cause noticeable colour changes in the most stable films and very noticeable changes in the least stable. Record slides have a very short life expectancy if they are also projected.

Underexposed films had better stability, and remain useful when some colour has been lost. Overexposed films had poor stability, and some lost colour rapidly as well as showing a colour shift as they faded. Slower films were slightly more stable. There were no significant differences between daylight/tungsten and professional/non-professional films.

For display purposes, the lifetime of transparencies can be improved by using an ultraviolet filter between the light source and the film.

### Acknowledgements

The work was carried out at Glasgow Museums, latterly with the cooperation of David Thomson and Pauline Ramsay, and with Dr Norman Peacock, Department of Pure and Applied Chemistry, Strathclyde University, and his students. All the films were exposed and the processing arranged by Davina Graham, photographer, Glasgow Museums, and the present director gave permission for publication. Several participants at the conference "Colour Imaging Systems", organised by the Royal Photographic Society at the University of Cambridge in 1986 made helpful comments when the work on accelerated ageing was presented there. Roy Perry, Conservation Department, Tate Gallery, commented on the manuscript.

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# Working Group 9

Textiles

Textiles





### Abstract

This project was a continuation of previous tests that determined that Orvus WA Paste is an effective agent in soil removal on wool and cotton. The tests compared the soil removal capabilities of surfactants used in textile conservation. The purpose of the current study was to estimate the optimum concentration of Orvus WA Paste for soil removal on cotton. This was achieved by measuring the cleanliness and amount of redeposition of soiled test substrates when washed in different concentrations of the surfactant. These differences were measured with the aid of a spectrophotometer. Results indicated by the parameters of this test concluded that a 1% solution gives the optimal cleaning.

### Keywords

Surfactant, anionic, Orvus WA Paste, concentration, cotton

## Report on Tests Performed to Determine the Optimal Concentration of the Surfactant Orvus WA Paste for Cotton

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### Introduction

The Textile Conservation Laboratory at Biltmore House has been conducting small in-house tests to investigate the efficacy of surfactants commonly used in conservation. The focus of these tests is to determine the most effective surfactants for our purposes and to determine the most effective procedure for their use. The first test, executed in 1990, compared the soil removal capabilities of "conservation-appropriate" surfactants. The results of that investigation were printed in the *Postprints of the Joint Session of the Painting and Textiles Specialty Groups* from the 1991 Annual Meeting of the American Institute for Conservation. The second report, which was published in the *Canadian Textile Conservation Newsletter*, Number 22, Spring 1992, discussed soil removal capabilities of Orvus WA (washing agent) Paste at different concentrations on wool. The following test report is on the soil removal capabilities of Orvus WA Paste at different concentrations on cotton.

Previous tests comparing the soil removal capabilities of surfactants determined that Orvus WA Paste is an effective agent in soil removal on wool and cotton (1). Percentages used by conservators, as stated in the conservation literature, vary greatly (2-7). Proctor and Gamble's product literature recommends adding 1-3 ounces to each gallon of water (approximately 0.77% to 2.30% concentration range) (8). The percent concentration of a surfactant is relevant when attempting to obtain the critical micelle count (CMC) in order to achieve the maximum cleaning benefits (9).

Orvus WA Paste belongs to a group of anionic surfactants known as sulfated linear primary alcohols (10). Orvus WA Paste is to be distinguished from the broad range of Orvus named products (11). These anionic surfactants are produced from sulfated coconut oil or sulfated tallow alcohols. Sodium salts are the most common type of sulfated linear primary alcohols. Sodium lauryl sulfate is used in low temperatures for delicate fabrics.

The positive characteristics of the sulfated linear primary alcohol types of anionic surfactants are the foaming and wetting capabilities, stability over a wide pH range, and biodegradability (12, 13).

### Test method

To begin the investigation, a test method was devised which would simulate known methods of wet cleaning used in textile conservation. It was based on certain practices of the textile industry that were applicable to the wet cleaning of historic textiles in addition to the practices of our and other textile conservation laboratories (14-16).

The main focus of this test was the variance in percent concentration. The factors which remained constant in this test include temperature, actual washing time, and the degree and amount of agitation (17).

### Concentration tests

The following concentrations of Orvus WA Paste were tested in this order: 0.1, 0.15, 0.2, 0.5, 1.0, 1.25, 1.5, 1.75, and 2%.

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### Testing procedure

The pre-soiled test samples were obtained from Testfabrics, Inc. These samples were first developed for the Navy during World War II. They were designed to test detergents which would be used on white cotton and denim where the solvent would be salt water. The main soil concerns were grease, oil, and soot from furnaces. The substrates, obtained from Testfabrics, Inc., were 100% cotton. They consisted of a soiled portion and a unsoiled portion. The standard soil media consists of the following components:

1.3% Keltex (Thickener)	1.7% vegetable fat (Spry)
2.2% cornstarch	0.3% butanol
72.4% water	4.4% Solvesso 150
14.0% oil (Mineral)	0.7% ethyl cellulose
0.42% oleic acid	0.7% carbon black
0.36% morpholine	
Total 98.48%	

The standard soil media was printed on the 7.5 inches wide substrate yardage in a pattern measuring 3.75 inches wide by means of an engraved print roller. The printed substrate was dried and heat cured using an electrically heated oven (18). The substrate was cut into samples measuring 7.5 inches long by 4 inches wide.

Spectrophotometer readings of the samples were performed before and after washing. To determine the results of the surfactant tests, a spectrophotometer (or more simply a spectrophotometer that is employed as a tristimulus colorimeter) was used. This type of machine calculates CIELAB color measurements and supplies a computer readout with these values and their interpretation (19, 20). The spectrophotometer used was a computer operated, high speed, high resolution scanning single beam ACS Spectro-Sensor II, housed and operated by BASF Corporation's Analytical Services Physical Testing Lab in Enka, North Carolina. The main concerns were with the change in the lightness and darkness ( $\Delta L$  or  $\Delta L$ ) of the soiled and unsoiled portion of the soiled substrates. Readings of the soiled area provide a measurement of the soil removal ability of the surfactant. Readings of the unsoiled area provide a measurement of the redeposition of the soil. The soiled testcloth samples were read by the spectrophotometer before and after wet cleaning. The samples were compared to themselves before and after rather than being compared to a color standard. The test results are based on the color difference between themselves. Each sample was its own standard.

A 10-liter pot of deionized water was set to simmer for use in subsequent steps. Shallow plastic wash trays, similar to the those used in photographic processing, were used in order to totally immerse the samples and allow enough room for agitation. The sample was immersed in about 1 inch of water (2 liters). For each washing, the samples were presoaked in a bath of deionized water at an average temperature of 35°C for 10 minutes.

The pH of the presoak bath with the sample was tested and recorded. The surfactant was mixed with 2 liters of deionized water to produce the 9 selected concentrations. The temperature was maintained at an average of 35°C. In some cases, the solution was heated on the stove to maintain a steady temperature. The sample was removed from the presoak bath and the used water was discarded from the tray.

The surfactant solution was poured into the same wash tray and the presoaked sample was immersed into the solution. The sample was agitated continuously for 5 minutes by gently pressing the solution into the sample with natural sponges. For the remaining 12 minutes, the sample was agitated periodically. The sample remained in the surfactant solution for a total of 17 minutes.

The sample was immersed in 2 liters of fresh, deionized rinse water which maintained an average temperature of 35°C. The sample was then slowly agitated in the rinse water for 3–5 minutes. A repeat rinsing was performed. The sample was removed between rinses. After the third and final rinse bath, the sample

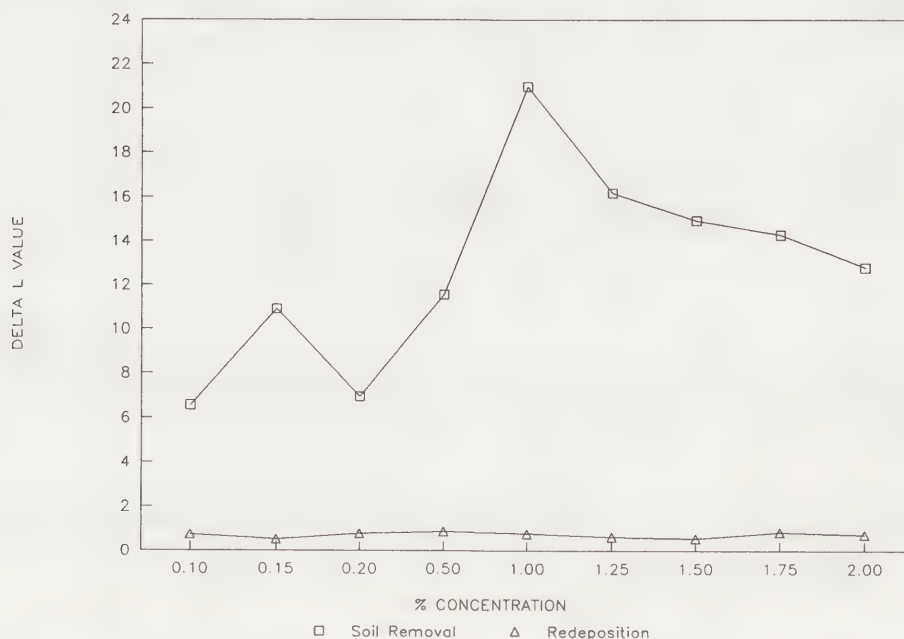


was removed and placed on a terry cloth towel and allowed to air-dry. The tray was washed between each surfactant test and each step.

### Test results

Spectrophotometer readings were taken of the soiled and unsoiled portions of the soiled testcloth substrates. The readings measured the difference in the lightness and the darkness ( $\Delta L$ ) of these areas.

The difference measured in the soiled portion of the substrate indicated the level of soil removal. The difference measured in the unsoiled portion of the substrate indicated the level of redeposition. The following graph illustrates the differences for each concentration of surfactant.



On the basis of  $\Delta L$  (lightness/darkness) values only, the tests show a steady increase in soil removal from 0.1% concentration to 1.0% concentration, except for 0.15%, which shows an unusual jump. This could be due to inconsistencies in the cleaning method, i.e., sponging application, or excessively aggressive hand agitation. A steady decrease in cleaning is observed from 1.0% to 2.0%.

The most unusual part of the test for both the wool and cotton tests was the irregular change in the lightness of the unsoiled areas of the substrates (21). All of these areas do read cleaner; in other words, they exhibit positive  $\Delta L$  values. If redeposition was a factor,  $\Delta L$  would be negative. However, the cleanliness readings of the unsoiled portions of the substrate do not coincide with those of the soiled portion. It is possible that these readings are too small to be of any significance in determining redeposition. This supports the premise with which the soiled testcloth was conceived. A concentrated soil mixture that stains the fibers is needed in order to compare the cleaning powers of a detergent and/or surfactant. If the soil is capable of being totally removed, the effectiveness of the surfactant/detergent cannot be accurately measured.

### Conclusion

From these limited tests, it can be said that the 1% concentration of the anionic surfactant Orvus WA paste achieved the highest amount of cleaning. Additional studies involving scanning electron microscopy and energy disperse x-ray analysis will allow us to find out which part of the "standard" soil was removed. To make this type of test more conclusive, a greater number of readings must be performed in order to achieve a statistical basis.

### Acknowledgements

The authors would like to acknowledge the support of The Biltmore Company, Rachel Paar (Textile Conservation Intern), Dorothy C. Morrison (Tapestry Conservation Spe-

cialist), BASF Corporation and Diane Kent (Research Engineer), and Mary Ballard (Textile Conservator, Conservation Analytical Laboratory).

### Materials

Orvus WA Paste (sodium lauryl sulfate). Proctor & Gamble, Winton Hill Technical Center, 6071 Center Hill Road, Cincinnati, Ohio 45224, USA, telephone (513)983-1100.

Testfabrics Soiled Testcloths. Testfabrics Inc., 200 Blackford Avenue, P.O. Box 420, Middlesex, NJ 08846-0420 USA, telephone (908)469-6446.

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## Abstract

This study describes the wet cleaning facilities designed to minimise handling and maximise the efficiency in cleaning large textiles at the Textile Conservation Studios, Hampton Court Palace. Analytical methods, such as pH measurement and ultraviolet-visible spectrophotometry, are applied to the washing process. The monitoring of the detergent during washing allows informed judgements to be made concerning length of washing, rinsing, and extent of mechanical action required, and suggests the potential development of more scientifically controlled and effective wet cleaning of textiles.

## Keywords

Washing, large textiles, detergent monitoring, pH measurement, ultraviolet-visible spectrophotometry

## Detergent Monitoring during the Washing Process at the Textile Conservation Studios, Hampton Court Palace

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## Introduction

The most commonly accepted method of washing large, old textiles, such as tapestries, has often posed problems. The washing of tapestries at Hampton Court Palace has on certain occasions necessitated the construction of a temporary washbath in one of the palace courtyards, using planks of wood and polythene sheeting.

The job always took several days, involving a large number of staff in the preparation, washing, rinsing, rolling of the textiles, and organising of separate drying facilities. As well as being physically taxing, the bulk and weight of wet textiles demanded teamwork and strength. Despite the great care taken, the traditional method, by its very nature, necessitated considerable handling, which is always inadvisable for wet textiles, but seems unavoidable (1).

The wet cleaning of textiles requires a gentle detergent, yet enough cleaning power (whether this is obtained by mechanical action, the action of the particular wash solution, or a combination of both) to remove dirt from the surface of the textile (2). This should be accomplished while retaining the textile's natural composition and minimising loss of fibre and colouring matter.

The Textile Conservation Studios, therefore, set itself an ambitious task when it set about developing a system for wet cleaning large textiles that would fulfil these criteria, culminating in the development of the studio's unique washing facilities.

The potential of these facilities is being exploited in terms of analytical science. Although various wet-fastness tests represent a usual preliminary to washing, the correlation between detergent formulation and dirt removal has so far remained unclear, especially when working with damaged textiles.

The aim of this study is to examine the potential of analytical equipment in achieving an improved washing process in the context of the Studio's newly developed wet-cleaning facilities. Two methods to assess detergent removal and residual soiled solution are investigated: pH measurement and ultraviolet-visible (UV-vis) spectrophotometry.

## Facilities and washing method

The wash bath measures 11 × 7 m and, therefore, can accommodate most large textiles (See fig. 1). It is constructed from aluminium with an inner, aluminum grid platform. The stable grid formation distributes the textile's weight evenly, keeping the textile from sagging, and thereby preventing any distortions that could develop when the textile is wet.

A net is stretched tightly across the surface of the grid framework providing a smooth and relatively compatible surface texture. The net has a particularly high degree of porosity, making it a suitable surface on which to both wash and dry the textile. It is sufficiently open to 1) allow fast drainage when supporting the drying textile and 2) prevent dirt and detergent from becoming trapped under the textile while washing, which would allow redeposition to occur.

During washing, the textile is supported on the inner platform, which can be raised or lowered hydraulically during the various phases of the wet cleaning process and according to the combination of procedures that has been chosen.

A special feature of the washing apparatus is a motorised, moveable spray boom that can travel up and down the washing surface, evenly distributing the wash solution or rinse water. The velocity, as well as the height at which the boom is suspended above the object, can be varied, allowing the amount of water pressure applied through the sprays to be controlled.

The entire washing and rinsing process is carried out using large quantities of water processed by means of a reverse osmosis unit.

A particularly soiled textile may be given a period of full submersion in a bath to which the wash solution has already been added. Alternatively, the textile can be wetted out initially by spraying the wash solution onto its surface with the moving spray boom before the textile is submerged in the bath. A less dirty or very frail object could be washed and rinsed purely by using the spray boom. The individual spray jets allow an even distribution of detergent and a gentle but thorough cleaning action.

On more soiled textiles, some form of additional mechanical action such as gentle sponging may occasionally be necessary. This can be carried out from a gantry that can be moved up and down the bath. The washing procedure can be monitored from this mobile platform. Samples may be taken from any area on the surface of the textile.

When rinsing is completed, the platform supporting the textile is raised above the level of the bath and the water is drained away. The washing of a large tapestry may be accomplished in a total of two to three hours. Aided by fans, the drying process requires one to two days.

### Tests-monitoring technique

Formulation of a suitable wet-cleaning detergent is the scientist's main goal. This process requires a knowledge of the particular nature of the dirt, stain, or any other matter present (3). The role of the analytical laboratory is not only to provide this information, but also to predict the behaviour of a textile during and after washing.

A condition report evaluating the state of the textile, combined with the results of preliminary analytical tests, such as wet-fastness tests and colouring matter identification, allows specific detergent formulation. Indeed, some studies have shown the effect of washing on dyes and more specifically on mordants (4-6).

Although the commonly accepted method of wet-fastness testing gives a good indication as to whether the colour tested is fugitive or not, the determination of the pH is probably more important. Indeed, it is not only a prime factor in determining the state of a textile, but it is also one of the means by which a correlation between dirt, dirt removal, and detergent additives can be reached.

A series of pH measurements using a pH meter are carried out to determine the pH of the reverse osmosis water, pH of detergent before the washing process, and pH of the sample taken from the surface of the textile at different stages of detergent spraying. Accurate pH measurements allow comparisons to be made between the pH of the washing solution at the beginning of the spraying process and at each subsequent stage of the washing process. Initially, the pH often tends to become increasingly acidic as the textile releases various substances into the wash bath and then gradually it reverts to its original value as washing proceeds.

The second monitoring phase concerns the rinsing process. To minimise the removal of colour while improving the cleansing, it is essential to control the remaining detergent residues on the textile. In order to determine how many rinses are required, the percentage of detergent residues in the rinse bath solution is assessed. For this investigation, a UV-vis spectrophotometer is used. The instrument is set up to measure the wavelength range 200-600 nm in absorbance mode with a double beam and a scan speed of 5 nm/second. Reverse osmosis water is used as reference and to prepare the sample.

Each sample of the rinse solution is scanned and then compared with the detergent solution. The Studio's washing solution is formulated with Synperonic



N, sodium lauryl sulphate (SDS), ethylenediaminetetra-acetic acid (EDTA), and sodium carboxymethyl cellulose (SCMC). The absorbance peak of the solution is measured at  $274 \pm 2$  nm, which corresponds to one of the main absorbance peaks. A scan with the wavelength range of 200–600 nm was used because of the presence of various substances such as dirt, dye, or other matter that can eventually appear in the soiled rinse solution. A series of samples are taken at intervals throughout the washing process from specific areas of interest.

### Case studies

Two quite different objects have been chosen as case studies to illustrate this paper, a large 16th-century tapestry, *The Triumph of Bacchus*, and the tester from *The King's Audience Chamber Throne Canopy*. The process of monitoring the effect of washing on the two textiles remains the same despite the different cleaning approaches.

#### *The Triumph of Bacchus*

This rare 16th-century tapestry from Brussels was purchased in 1540 by Henry VIII and measures  $4.5 \times 7.2$  m. One of a pair, it derives from a set of grotesque tapestries woven from cartoons attributed by Vasari to Giovanni da Udine (7). It was transferred from Windsor Castle to the Textile Conservation Studios for conservation treatment prior to being displayed in the newly restored King's Apartments at Hampton Court Palace.

The object's importance, the fine quality of weaving, and the high proportion of silk and metal thread in its composition made it essential that the tapestry was washed with as little handling as possible. The tapestry was washed face up using the submersion facilities of the bath.

Wet-fastness tests did not show any significant bleeding of dyes. Dye analysis was carried out in order to provide historical data. Thin-layer chromatography using reversed-phase plates displayed a range of natural dyes such as madder, weld, indigo, tannin, and, in some cases, synthetic dyes (from restoration threads).

Metal thread analysis revealed a high proportion of copper and confirmed the choice of EDTA as a sequestering agent. The latter was preferred to sodium tripolyphosphate or sodium citrate because as well as increasing washing power and stabilizing dirt emulsion, it causes the least amount of copper removal.

The detergent formulation was as follows: 0.50 g/l of Synperonic N and 0.05 g/l each of SDS, EDTA, and SCMC. The bath temperature was 18°C. The pH measurements for the detergent and reverse osmosis water were 6.3 and 6.4, respectively.

A set of pH measurements were taken over a period of approximately 50 minutes while the detergent was applied by spraying. This was to ensure that the tapestry's surface was not affected by the release of dirt and to prevent the movement of certain dyes that could be sensitive to the acidic conditions that this could engender. The results are expressed in Figure 1.

The monitoring system involving pH and UV-vis measurements began from the second traverse of the spray boom. The entire washing process lasted approximately 1.5 hours.

It is particularly interesting that pH measurements obtained at the end of the rinse correspond to that of reverse osmosis water. Also, the semi-quantitative UV-vis analysis suggests that 0–2% of the original strength of the detergent remains in the final rinse water. Clearly, the two methods complement each other and provide information allowing the decision to be made to stop rinsing. This keeps both the length of the wet phase and the use of purified water to a minimum.

#### *The tester from The King's Audience Chamber Throne Canopy*

This canopy formed part of the original state furnishings prepared for William III's occupation of Hampton Court Palace (following Christopher Wren's building work at the palace, c. 1700). The tester is constructed from four pieces of

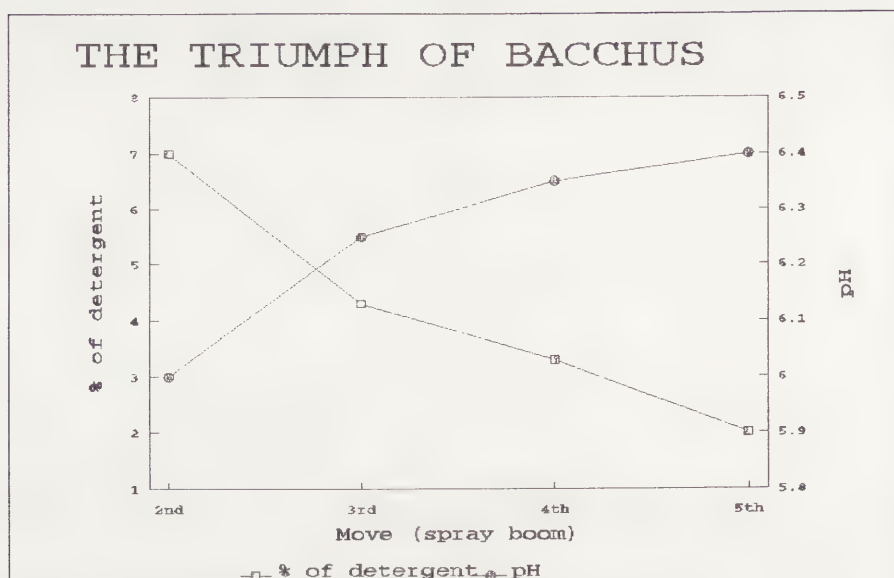


Figure 1. pH measurements during detergent application.

crimson silk damask, is backed by a plain weave adhesive-dressed bast fibre fabric, and measures  $2.5 \times 1.8$  m.

The throne canopy was rescued from beneath mounds of steaming rubble after the fire in the King's Apartments at Hampton Court in 1986. The textile components were ripped, charred, sodden with blackened water, and splattered with molten lead from the roof. The tester and all other pieces received an emergency wet clean using deionised water to help flood out quantities of grit. Despite this treatment and repeated surface cleaning, considerable foreign matter remained lodged between the damask and the linen backing and between the damask and gilt orricle lace decoration. The decision to use the spray boom facility was made in the hope of further eliminating foreign matter which still remained in the extremely weak and fragmented object. The tester was washed face up; the detergent formulation and parameters were similar to that of the "Bacchus" tapestry.

The entire washing process took approximately 1.5 hours in comparison with the previous washing of a similar relevant textile, which took three hours. Although this total time is arbitrary, it appears that the reduced length of washing time, along with minimum mechanical action, are appropriate for degraded silk objects.

Two major improvements in the wet cleaning of the textile were apparent. First, no long soaking treatment was necessary since the action of the spray, working straight through the surface of the object from front to back, was gentle and effective. Avoiding prolonged soaking was particularly desirable since it increases weakening of textile fibres. Secondly, the particularly effective action of the spray also meant the textile did not need to be reversed for washing on the back, thereby decreasing the risk of damage through handling it when wet.

It was difficult to take enough samples on the surface of the tester for pH measurements to be made because the spray wash technique was used in this case, as opposed to the full submersion technique used for the tapestry. Nevertheless, monitoring of detergent levels in the rinse water allowed us to calculate that 35 minutes was needed to reduce the amount of detergent in the rinse water to an acceptable level. The results are shown in Figure 2.

Even if the accuracy of these results is open to discussion, the tests still provide overall information about the presence of detergent over the textile surface. It is important to minimise the residual soiled solution that could accelerate the deterioration of either the silk or the bond between fibre and mordant/dye.

This particular wet cleaning process showed that the sampling method could



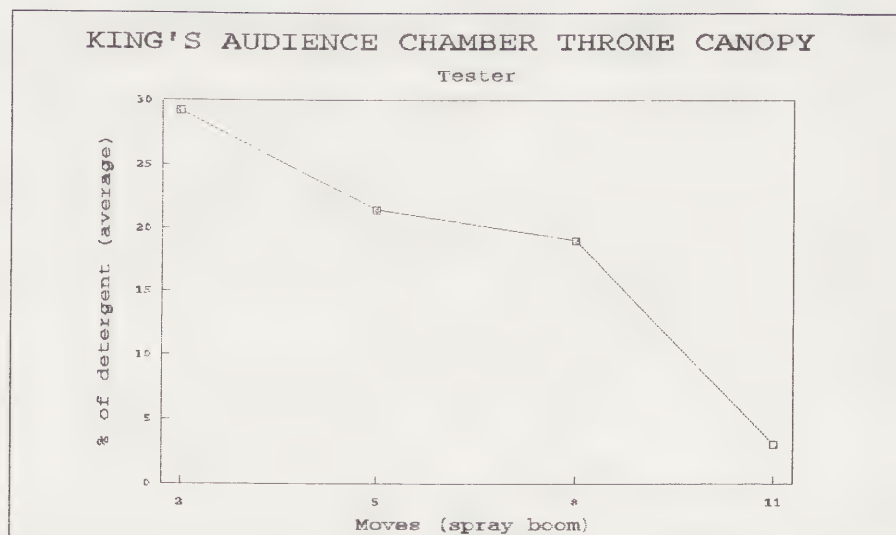


Figure 2. Monitoring of detergent levels in the rinse water.

be improved in order to collect enough solution for further pH tests. Taking samples with a help of a micropipette seems to be the ideal solution. However, this would not produce more accurate results, especially when washing textiles that have been netted over their surface for protection during wet cleaning since the net will trap dirt plus detergent to some extent.

### Conclusion

The combination of wash table facilities at Hampton Court Palace allows minimum handling and movement of large, frail, wet textiles. Even support is provided by a gridded surface. The textile can be submerged or spray-washed according to its condition. Sprays provide mechanical action which gently but effectively cleans the textile. The potential inherent in such equipment, along with the possibilities of analytical monitoring, represents significant improvements in the washing of old, large textiles.

Although additional mechanical action may sometimes be required when washing old, soiled textiles, the establishment of a monitoring system enables informed judgements to be made regarding the extent to which this is carried out, thereby minimizing the amount of mechanical action.

It is essential to determine the correlation between the nature of the soil, dirt removal, and detergent formulation; this investigation must remain the primary concern. UV-vis spectrophotometry, combined with pH measurements, considerably improves the ability to monitor the presence of detergent during washing and after rinsing.

The decisions regarding wet cleaning are based on the acceptability of results and require a balance between the following four considerations: concern for the condition of the textile, the length of time during which a textile can safely remain wet, achievement of the greatest percentage removal of detergent from the rinsing solution, and aesthetic considerations. Of course, tests are performed on samples rather than on the entire textile; generalisations can be made from the test results, but may not be completely accurate for the textile as a whole.

Monitoring could be developed further if visual interpretation of colour change could be correlated to instrumental measurements. The assessment of colour change and especially the ability to quantify the difference between brightness and chromaticity prior to and after washing could lead to improved treatment methods and washing solutions.

### Acknowledgements

Special thanks to Mr Jack Willard for designing and constructing the washing table (in consultation with Studio staff), Eurotech for advising on the installation of the reverse

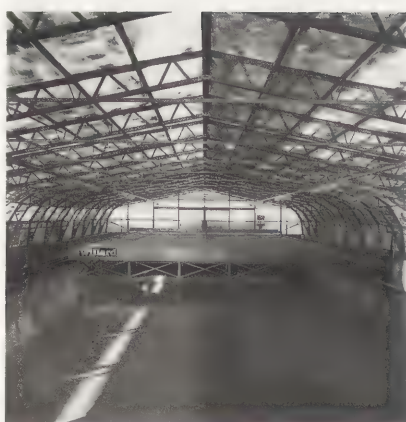


Figure 3. Wash table.

osmosis unit, and the Building Services Department of Historic Royal Palaces for modification and adaptation of the building.

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## Abstract

The paper concerns the restoration of an embroidered velvet chasuble that is part of the set of vestments of Cardinal Vanzi on exhibition at the Orvieto Cathedral Museum. The chasuble was presumably made in Florence at the end of the 15th century; the embroidery design has been attributed to Signorelli, Bartolomeo di Giovanni, and Botticelli. For identification of the methodology, preliminary investigations were carried out: graphic survey, microscopy, identification of dyes, analysis of metal threads by scanning electron microscopy (energy-dispersive spectroscopy), ultraviolet photography, radiography, and solvent testing to identify soiling. On the basis of these analyses, it was possible to remove the previous amateurish restoration which had contributed to the deterioration of the object. After dismantling the chasuble, the velvet was restored by a full cloth support consolidated with couching stitches; the embroideries were restored on a full cloth support and consolidated with stitches selected on the basis of the results of the preliminary investigation. The intervention was consistent with the visual and structural characteristics of the object and still easily identifiable and reversible.

## Keywords

Chasuble, graphical survey, microscopy, dye analysis, metal threads, scanning electron microscopy (energy-dispersive spectroscopy), ultraviolet photography, radiography, solubility test, velvet, couching stitch, cloth supports

## Restoration of the Chasuble from the Vestments "Vanzi" of the Orvieto Cathedral

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## Introduction

The restored chasuble is on exhibition at the Orvieto Cathedral Museum (See fig. 1). Together with two dalmatics, a stole and two maniples, it is part of the set of vestments worn by Cardinal Sebastiano Vanzi during the Council of Trent in 1563. This set of vestments, however, is of an earlier date and was presumably made in Florence in the last quarter of the 15th century (1–3).

The designs for the embroidery have been attributed by various experts to Signorelli, Botticelli and Bartolomeo di Giovanni (4–9). The vestments are believed to have been created to order for the Orvieto Cathedral, as the saints depicted on the chasuble include the patron saints of the city, St. Brizio, St. Costanzo, St. Faustino, and St. Pietro Parenzo.

Few other records exist on the history, origin, movements, and restoration of this article (10). At the beginning of the present century, the chasuble, already in the museum, was exhibited in Italy and abroad on a number of occasions (3, 4, 11–13). It has also been mentioned in many publications on the history of fabrics.

The Vanzi vestments are of red, pile-on-pile, silk velvet, with areas of bouclé pile, on a taffeta tabby, the warps and wefts in yellow silk support a patterned weft in metal thread. The pattern of the velvet was known as "griccia" in the terminology of the time; the pomegranate motif is surrounded by a palm with eight lobes held aloft by a undulating trunk (14). The embroidered columns of the chasuble enclose the figures of nine saints enthroned in niches: the Virgin Mary, St. John, St. Paul, St. Andrew and St. Brizio (a bishop) on the front; St. Peter, presumably St. Costanzo, St. Faustino, and St. Pietro Parenzo on the back.

The materials used for the embroidery are silk and metal-wrapped threads (gilded silver strips wound on silk thread). The embroidered forms are surrounded by green silk ribbons. Pieces of paper from different periods are pasted to the back of the embroidery. Twenty-five different stitches and techniques are used in the embroideries, the most common of which are shaded gold, split stitch, satin stitch, and couching stitch. The architectural elements and borders are embroidered on the linen cloth on which the designer drew the original patterns in ink; in the centre of the niches, unembroidered spaces were left for the saints which were executed separately.

The shape of the chasuble is rather irregular and atypical, suggesting that it may have been adapted from a cloak chasuble (*casula*) by removing the sides.

## Condition

The condition of the chasuble was very poor. There were large holes in the shoulders caused by the coat hanger; the holes were patched with velvet. The entire garment was very soiled. It had been on display in the museum for a century without any protection from light, and was faded and crumbling. There were cuts in the direction of the warp, raised metal threads. The pile of the velvet was missing in places, flattened in others, and soiled with wax, rendering the embroidered designs almost unrecognizable. This situation was aggravated by a previous attempt at restoration with coarse thread that united the velvet, embroidery, and the blue lining, making large areas rigid, and interfering with

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Figure 1. Front side of the chasuble before the restoration work.



Figure 2. The chasuble during the restoration work, photographed with grazing light.

the fall of the fabric (See fig. 2). Not all the damage had been repaired, suggesting that deterioration had continued after these restoration attempts.

From the beginning of the project, it was decided to see whether this amateurish restoration work could be removed. It was also hoped that materials could be identified, as well as the period in which it was performed. Before any work could be done, it was essential to acquire detailed knowledge of the techniques used in the creation of the article, especially the different layers and seams. Several methods of investigation were used, with the help and support of the director of the project. Although the results of these studies were only preliminary, they confirmed the utility of scientific methods of investigation in the restoration of fabric articles.

### Graphical survey

The article was first copied full-scale onto acetate. The drawings were reduced photographically, and different versions were prepared indicating condition, techniques, and previous restorations (See fig 3). When restoration was complete, an additional version was prepared detailing the methods used.

The initial examination of the article indicated that the vertical cuts and abrasion of the velvet were situated in areas not restored in the 19th century, and that this amateurish restoration had made the areas rigid this has caused tensions in the cloth, raising neighbouring areas. All damage to the velvet, including cuts, raised weft, and abrasions, was due to weakening of the warp.

### Chemical and physical analysis

Fabric samples were examined with a microscope using reflected light (100× magnification). The velvet was found to have silk warps and wefts; the fibres were deformed from their characteristic cylindrical shape, showing breakages and encrustation. The threads used in the 19th century restoration were in even worse condition.

Identification of the dyes was performed with the aid of light microscopy, qualitative microchemical and physical investigations, solvents testing, reagents and mordants, and examination with ultraviolet light (UV) (performed by Dr. A. Bensi). The red restoration thread was dyed with fuchsin, first used in the 1860s, and the yellow thread was dyed with quinoline and uranine, first used after 1885. The dyes identified in the velvet were *Reseda luteola* L. for the yellow weft, a natural dye not identified with certainty, perhaps *Oricello* (a red extracted from lichens like *Rocella tinctoria*) for the red warp. The older green ribbons were dyed with *Reseda* and indigotin, a dye extracted from *Indigofera tinctoria* (indigo) or *Isatis tinctoria*.

Metal thread analysis was performed with scanning electron microscopy energy-dispersive spectroscopy (using a Cambridge Stereoscan 250 SEM, Link Analytical microprobe, and computerized 860/500 system) at the Centre for the Chemico-physical Study of Synthetic and Natural Macromolecules, CNR, Genoa (operator G. Dondeco, supervisor Prof. E. Pedemonte, coordinator Dr. P Bensi) (15–20).

The following information was learned about metal thread specimen D1 from the velvet of the dalmatic: width, 230  $\mu\text{m}$ ; left-hand torsion; mean winding density of metal strip, 3 segments/mm. The metal composition was 45–46% gold, 43% silver, and about 4% copper (cf. specimen E1). The condition of the specimen was good.

The following information was learned about metal thread specimen E1 from the velvet of the chasuble: width, approximately 295  $\mu\text{m}$ ; left-hand torsion; mean winding density, 1.5 segments/mm. The condition of the specimen was good. X-ray spectrometry and semi-quantitative analysis revealed a composition of 47% silver, 41% gold, and 5.5% copper. There was a small amount (3.7%) of chlorine.

The following information was learned about metal thread specimen D3 from the embroidery of the dalmatic: width, 230  $\mu\text{m}$ ; left-hand torsion; mean winding





Figure 3. Graphic survey of the condition of the chasuble. Black areas indicate restoration carried out in 1890.



Figure 4. Radiography of the embroidered figure of St. Paul.

density, 1.5 segments/mm. The condition of the specimen was good. X-ray spectrometry of the inner and outer faces was performed separately. Semi-quantitative analysis revealed 81% silver, 14% gold, 3% copper, and 0.87% chlorine on the outer face, and 96% silver, 2.7% copper, and 0.96% chlorine on the inner face.

### UV Photography

The UV sources were fluorescent tubes. The areas of the velvet and embroideries in which the metal threads were missing were clearly visible as dark patches under UV light. The threads of the previous restoration showed up with strong white fluorescence. The red and blue silk, apparently homogeneous to the naked eye, revealed differences in fluorescence under UV. On the niches and the figures of St. Peter, St. Andrew, and St. Brizio, a dark silk thread used to define shaded areas was revealed; this shading was imperceptible under normal light.

Other UV photos taken after the saints had been unstitched showed that the vertical midline of the tabby on which the embroidery was performed had been marked by plucking a taut thread stained with charcoal. Ink lines of the original drawing and writing with the name of the saint (almost illegible under normal light) were also revealed. Dark areas on the surface of the linen tabby indicated the penetration of glue from the opposite side.

### Radiography

Investigation was performed with a 3 kW, 5 mA Gilardone apparatus using Kodak film and two to three minute exposures (performed by technicians of the ICR, Rome).

Much information was obtained about the quantity, type, and deformation of the metal threads, and about the overlapping of embroideries and velvet. For example, the figures of the Virgin Mary and St. John cover a long strip of the figure of St. Peter that has been cut, and cover a large area of velvet. In the figure of St. Brizio, the lower edge is folded under but almost intact. All the edges of the saints overlap the surrounding embroidery. Hemp cords were observed under raised borders, and paper under all the embroideries. It was also possible to visualize the linen lining at the back of the chasuble (See fig. 4) (21).

### Dirt identification with solvent testing

Many tests were performed on the surface of the embroidery and velvet with different solvents. The most effective were found to be hexane and white spirit, suggesting that apart from dust, the layer of dirt was of a greasy nature.

### Results of investigations

To summarize, the most interesting information emerging from the investigations preliminary to restoration were that the surface of the chasuble was highly deformed, mostly due to a previous restoration attempt. All the metal threads are of the beaten gold type, that is, thin strips of silver gilded on the outer surface; the silver is not pure but alloyed with copper. Metal threads are missing from the entire surface of the article; the extent of this loss can be quantified with UV photography. There is much overlapping, and paper was found pasted to the back of the embroidery. The materials have become very fragile with age. Many previous restorations are evident, the most extensive and recent of which was probably executed between 1885 and the beginning of the present century. This date is possibly confirmed by the fact that the Orvieto Cathedral Museum was founded in 1890; the restoration of the articles on exhibit was probably performed at that time.

### Conservation and restoration

The first step involved cleaning both sides of the article by vacuum suction. A bigger and more powerful vacuum cleaner was used for the lining and velvet, while a polyester gauze protected their surfaces; a micro-vacuum cleaner was





fig. 5a




-  —Background of the embroidery (linen tabby)
-  —Embroidered columns (metal threads embroidery)
-  —Figure of Saint (metal threads embroidery)



fig. 5b





-  —Background of the embroidery (linen tabby)
-  —Embroidered columns (metal threads embroidery)
-  —Figure of Saint (metal threads embroidery)
-  —Further support (linen tabby)

Figure 5. Support placed between the embroidered figures and the embroidered background.

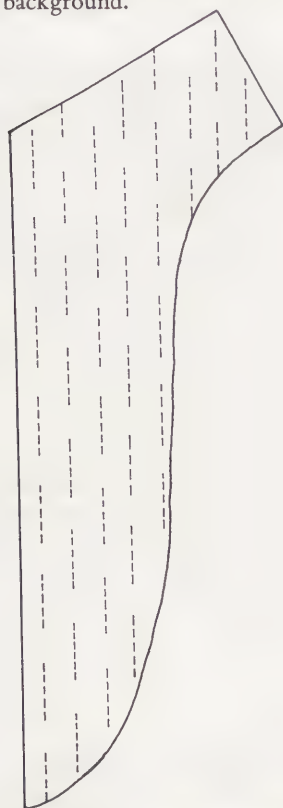


Figure 6. Running stitch on velvet.

used for the embroideries. This operation was performed very quickly because of the fragility of the fibres.

Next the article was dismantled, starting with the much deteriorated green ribbons. During this operation, underlying ribbons were discovered. These were documented with drawings and photos, and measured exactly. Once the ribbons had been removed, the underlying area was unstitched from the velvet, moving in direction from the shoulder to the hem. In order to detach the chasuble completely from the lining, it was necessary to remove the stitches of previous repairs. The threads were cut with a scalpel and removed with scissors and tweezers on the lining side or between the lining and the velvet. In this way, it was possible to avoid stretching and manipulating the right side of the embroidery and velvet. The paper found under all the embroideries had been degraded by silverfish and showed cracking and swelling due to humidity. Since the paper could have prejudiced the future conservation of the article, it was removed. This was easily done, taking advantage of the cracks and with the help in some places of a solution of methylated spirit in water; the pieces were then repositioned on a drawing of the article to aid future restoration attempts. Finally, the embroidered figures of saints were detached from the embroidered backgrounds.

Before consolidation, the ribbons were cleaned on absorbent paper with a cotton pad moistened with white spirit. Since the ribbons had been twisted out of shape, they were arranged on cork covered with Melinex and held in place with entomology pins and glass weights light enough to allow rinsing. Due to the fragility and distortion of the ribbons, this operation was accomplished with water, glycerine and alcohol. The ribbons were measured before and after this operation to confirm that shrinkage did not occur.

Both needle and adhesive techniques were used for consolidation. A support of dyed silk tabby was heat bonded to polyester gauze (Stabiltex Tetex PES-4/TR) treated on both sides with polyvinyl adhesive (Mowilith DMO2/DM5 25/5% in water). The ribbon was then attached to this support and reinforced with couching stitches using Gutterman polyester thread. This type of support enabled gaps to be filled during reassembly. Only the lower (i.e., older) layer of ribbons was reassembled. The other ribbons had probably been added to cover gaps in pre-existing ribbons.

The embroidered backgrounds were cleaned using cotton pads moistened with dry cleaning fluid. The saints, which were in better condition, were cleaned by immersion. This method was adopted on the basis of assay results showing the greasy nature of the dirt. After cleaning, the embroideries were arranged, the twisted gold threads straightened, and the silk tabby mounted on frames. The frames had been prepared with dyed linen supports having a fibre density slightly less than the embroidered material. The same procedure was followed for the figures, but the heads and the bodies were mounted separately on different frames since they had originally been executed separately. In mounting the pieces on the frames, warps and wefts were arranged on the straight, starting from the centre of the embroidery, which was easily identified from the original drawing of the embroidery on the cloth.

The stitches used for consolidation were selected on the basis of the results of the preliminary study of the types of stitches originally used in the embroidery. The stitches we used to fix the lifted metal threads were similar to those of the original; this decision was made so that the patterns would be intelligible. However, the new stitches are easily identifiable because of their slightly different colour and finer thread. The polyester thread used also has a specific fluorescence when photographed by UV light and can therefore be distinguished from all the other threads. This technique of consolidation was chosen because any other type of neutral and uniform stitch would have flattened the images and destroyed the almost pictorial character of the article.

Some of the dark threads surrounding and emphasizing the figures were replaced, but only when the underlying original drawing was legible or when traces of the original threads were still present.





Figure 7. Front side of the chasuble after the restoration work.

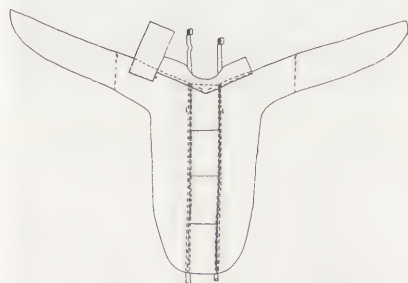


Figure 8. Process of reassembling work.

At the end of these operations, the embroideries were removed from the frames and arranged for reassembly. During this treatment phase, an additional support, i.e., a piece of linen, was placed under the figures in order to prevent differences in thickness between the embroidered backgrounds and the figures (See figs. 5a, 5b).

The velvet was lightly steamed after checking the pH. Steaming was especially necessary in the folds of the fabric where previous restoration had been undertaken. These parts were then brought back into shape with the help of water and methylated spirit. The parts in velvet were then placed on the support of dyed silk and stitched to it from top to bottom with a running stitch (See fig. 6). The gaps were consolidated with a couching stitch. All the work was carried out with curved needles on a table. Before reassembly, the lining was washed in water containing 2 g/l Ultravon, 0.5 g/l sodium citrate and 0.005 g/l sodium carboxymethyl cellulose. The lining was then arranged and consolidated where necessary with patches of linen and couching stitches. Reassembly was carried out on a flat table with curved needles utilizing all the information noted in the initial graphic survey. The dismantling steps were followed in reverse order. Two additional strips of herringbone twill were used to reinforce the seams between the velvet and embroideries. These strips had substantially the same role as the supports of the green ribbons (See figs. 7, 8).

### Dyes

The dyes used in the restoration were of the type Lanaset CIBA for silk and Solophenyl CIBA for linen. In choosing the colours, we sought a neutral colour for the areas where material was missing, taking the colour of the threadbare areas into account, since in the process of deterioration, threadbare areas precede holes.

### Conclusions

In conclusion, the aims attained in this restoration work were twofold. The first aim was to remove the main causes of degradation of the chasuble and to make the patterns intelligible, in view of the almost pictorial character of the article. This was attained by methodologies selected on the basis of scientific preliminary investigations. The second aim was to select a type of treatment intervention that was consistent with the visual and structural characteristics of the object and which was, at the same time, easily identifiable and reversible.

### Acknowledgements

The restoration was financed by the Umbrian "Soprintendenza per i Beni Ambientali, Architettonici, Artistici e Storici" and was directed by Dr Giuseppina Testa. The work was performed in the COORECTA laboratories, in Spoleto with the assistance of Lory Cucchiaroni.

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## Abstract

Microbial attack on an ancient textile was examined before restoration. Biodeterioration agents were identified and assessed using cultural analyses, microscopy, and firefly bioluminescent assays of ATP. Textile fibres were identified with microscopy and microchemical tests. The results of these studies allowed us to verify that the textile artefact was a mixed weave, and that the morphology of alteration was directly related to microfungal attack on the different textile fibres. The efficacy of two different biocides was tested; the biocides chosen were among those most frequently used for the disinfection of textile materials.

## Keywords

Textile conservation, silk, cotton, linen, fungi, biodeterioration, biocides

## A Case of Fungal Biodeterioration on an Ancient Textile

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## Introduction

Textiles, particularly those of historical and artistic value, are very susceptible to microbial attack (1–5). The growth of active agents on textiles and the subsequent deterioration depends on the microclimatic conditions of the environment and on the fibre type. Consequently, biodeterioration can appear in several forms; different kinds of staining may be observed, and the textile may undergo losses of strength and material (6).

Fungi are the most frequent among biodeterioration microorganisms in textiles. The environmental conditions required for fungal growth (RH 65%, temperature  $\geq 20^{\circ}\text{C}$ ) are very often found in sacristies, museum storage conditions, other storage facilities, churches, and other locations. It is common knowledge that the cellulosic fibres are more liable to the fungal attack than those comprising protein (7).

In this research, a microbial alteration was studied in a 19th century damask-made dalmatic, an ecclesiastical outer vestment. The morphology of the alteration was typical of microbial attack with the appearance of differently-shaped dark spots. There were two main types of stains: one was superficial, diffused, and had a greyish color (type A), while the other was located deep within the textile, and was smaller and darker (type B) (see figs. 1–3). Two different biocide products, chosen from among those most commonly used in the textile conservation field, were tested (8–10).

## Materials and methods

The artefact was observed under the stereomicroscope, and the samples obtained from the two types of alteration were analysed microscopically in order to accurately define the nature of the deterioration.

Samples were taken by rubbing sterile cotton swabs on the two different types of stains. The collected material was put on cultural medium surfaces (Myco-logical agar—DIFCO) in petri dishes. Thus prepared, the cultures were incubated at  $28^{\circ}\text{C}$  for seven days (until growth of the colonies was observed). The developed fungi were isolated in pure culture on slants of the appropriate media (Czapek Dox agar—DIFCO). The identification of fungal species was performed according to standardized methods by consulting the appropriate manuals (11, 12).

The microbial adenosine triphosphate (ATP) was evaluated on suspensions of specimens collected from two alterations, using Biocounter M 2500 (Lumac) and conventional reagents included in the Hygiene Monitoring Kit n.9292-7 (Lumac). The results were reported in Relative Light Units (RLU) that corresponded to the ATP level present in the samples (13).

Textile fibres were identified microscopically by examining the morphological structures. Small fragments of weft and warp threads were transferred to slides and examined microscopically, using transmitted or polarized light (crossed polars) (14, 15). Microchemical analyses were also performed using staining reactions (standard methods, ASTM D276–77) and differentiated solubility tests (16). For the solubility tests, the fibres were immersed in cold nitric acid (17).

The biocides chosen were chosen from among those most commonly used and considered most effective in the treatment of fungal attack on textile materials. Two BAYER products, Preventol O (R) (o-phenyl-phenol) and Preventol CMK

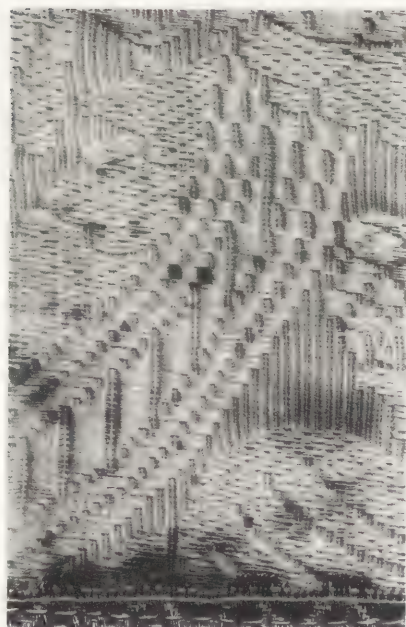


Fig. 1. Detail of textile, showing alterations due to microfungal attack.

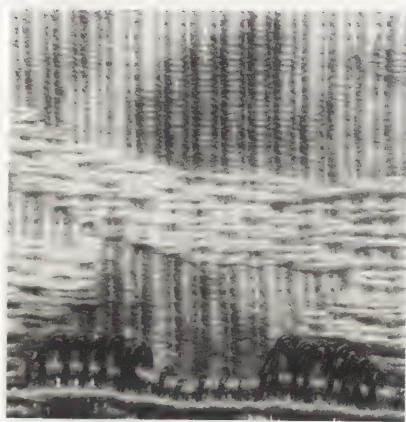


Fig. 2. Superficial, diffused and grey-coloured alteration (type A).

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(R) (p-chloro-m-cresol in aqueous solution at 1%) were used by brushing. Cultural analyses were performed a week after treatment for an evaluation of efficacy.

### Results

In the preliminary microscopic observation, the reproductive structures of the genera *Aspergillus* and *Penicillium* were detected on the type A stain; spores and perithecia fragments of *Chaetomium* sp. were observed from type B stain (see fig. 4). The results of cultural analyses show good development of fungi from type A, and absence of growth in the plates made from all samples collected from type B stains. Those results are apparently in contrast but the ATP evaluation provides an explanation (see table I).

The fungal attack is not active on black spots. Consequently, although traces of fungal structures were visible under the stereomicroscope and the optical microscope, the results of the cultural analyses were negative. Instead, the fungal attack is still active in the greyish stains, as confirmed by the cultures and ATP evaluations. The species isolated in culture were identified as *Aspergillus flavus-oryzae* and *Penicillium chrysogenum*; the first species was the most recurrent in all cultural plates, so the second species can be considered a contamination. As to fibre identification, the weave of the artefact was identified as a weave made of silk weft threads, and cotton and linen (in the ratio of 9 to 1) warp threads (see fig. 5). Both the biocides tested were equally effective.

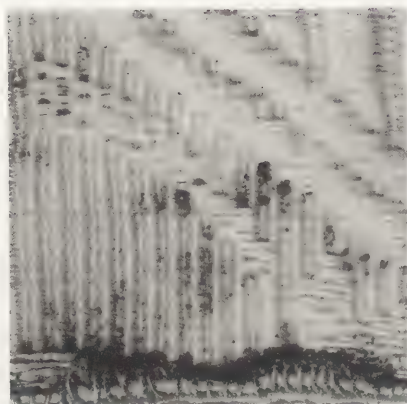


Fig. 3. Located deep within the textile and black alteration (type B).



Fig. 4. Microphotograph of a sample detected from the stain B, showing hair fragments of *Chaetomium* sp. (magnification 16×).



Fig. 5. Microphotograph of cotton and linen fibres from a warp thread (10×).

Table I. Results of cultural and ATP analyses.

Sample no.	Alteration	Cultural analyses	ATP (RLU)
1	greyish stain	+	1914
2	greyish stain	++	2566
3	black stain	—	59
4	black stain	—	67
5	no alteration	—	40

— = absence of growth; + = light growth; ++ = medium growth; +++ = heavy growth.

### Conclusions

From an overall evaluation of the results it can be asserted that the microbial attack varies according to the nature of the fibre. Indeed, the alteration which appears as a superficial greyish stains is related to the development of *Aspergillus flavus-oryzae*; this species of fungus shows protease activities. Members of the *Aspergillus flavus* group are commonly cultivated for their production of proteolytic enzymes. For example, they are employed in the degumming of silk (18). The attack by this fungus on the textile was localized on the protein weft threads, and is still active.

With regard to the black stain, the alteration is caused by the development of *Chaetomium* sp.; cellulolytic activity is characteristic of this genus. In this case, the warp threads are involved in the attack. The growth of this fungus and the consequent distribution of alteration are related to the type of weaving. Unlike the former, this attack is not active. The viability of microorganisms depends, other than on the nature of the substrata, on environmental conditions. In this case, the environmental factors, which at first favoured fungal development, become unfavourable because the conservation site had been changed. This situation could have reduced the degree of viability of the biological agents; in particular, it prevented *Chaetomium* sp. from developing.

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## Abstract

The evolution of space suits from the 1930s through the 1970s demonstrates the remarkable growth in aerospace technology. This paper gives a brief description of the suits in the American collection, causes of their present state of degradation, conservation treatment plans, and conservation research into the organic causes of their degradation.

## Keywords

Space suits, aerospace technology, conservation treatment, modern textiles, high technology



Figure 1. Apollo AML Pressure Garment Assembly. Cut-out reveals pleated pressure bladder and liquid cooling garment. NASM archives photo #92-616.

## Space Suits, a Legacy of America's Space Program: Their Evolution and Conservation Problems

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## Introduction

Stored in an environmentally controlled room at the Smithsonian's Paul E. Garber Preservation, Restoration and Storage Facility are suits representing all phases of aerospace development. Modern space suits evolved from pilots' flying clothing, which had developed greatly from the early days of flight. For example, the first American pilots, Orville and Wilber Wright, wore nothing more protective than business suits during their first flights in 1903 because the Flyer only rose a few feet above the ground (1). In contrast, a functioning space suit is something like a personal spacecraft for protection of humans in the hostile and deadly environment of space. Space suits supply breathing oxygen and an envelope of pressure around the human body (See fig. 1).

## Early suits

Special flight clothing and personal equipment needs for World War I triggered necessary research in human physiology and aviation medicine. Since the planes of that time generally reached altitudes of only 10,000–15,000, pilots merely needed protection from the cold. Brown leather flying coats over regular olive-drab wool uniforms were standard clothing for United States Army pilots. They also wore either leather riding boots or high-top service shoes and leggings. For head protection, they wore hard, leather football-type helmets with goggles.

As planes became able to reach higher altitudes, oxygen masks became necessary to compensate for the thinner air. In the mid-1930s, the Aero Medical Laboratory began developing equipment to counteract the physiological difficulties experienced by crewmen using the new fighters and bombers with supercharged engines. These planes could fly above the limits where conventional oxygen equipment protects humans (between 10,000 and 40,000 feet). Above 50,000 feet, because of lowered air pressure, it becomes very difficult to push oxygen into the lungs. Greater than the threat of oxygen deprivation is the effect of such low pressure on a human body; it causes fluids to vaporize at body temperature. Bubbles form from body gases and block circulation; death results in ten seconds. The development of pressurized cabins and suits solved these problems.

Pioneer aviator Wiley Post became the first American to use a protective pressure suit, flying in the lower reaches of the stratosphere in cross-country speed flights. Post's high-altitude suit, designed by Russell Colley of the B.F. Goodrich Company in Akron, Ohio, was a human-shaped rubberized gas bag molded in a sitting position and protectively enclosed in sailcloth (2). This suit greatly inhibited movement while pressurized, since any bending of the joints caused a change in volume, and therefore pressure, inside the suit. The force to change this pressure had to come from the wearer; this made moving and holding one's arms and legs in certain positions grueling work.

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By the 1950s, higher and faster flying jet and rocket-powered planes began to nudge the edge of space. Many different types of researchers now studied the physiology of humans in high flight. Emergency partial pressure suits were being developed as backup for pilots in case of sudden cabin depressurization. The suit was a combination of a nylon inflatable vest and rubber tubes, called capstan, sewn along the sides of the arms, chest, and legs that pulled the suit's fabric tightly around the wearer. This applied mechanical counter-pressure against internal expansion of gases and water vapor in blood vessels and tissues at high altitudes (3).

In the 1950s, a successful, full-pressure suit emerged from the combined innovative efforts of the U.S. Navy, the Aero Medical Laboratory, and private industry. Russell Colley, who made Wiley Post's 1930s suit, greatly improved suit mobility by the use of narrow accordion-like pleats sewn into the arms and legs. It was inspired by observing the convoluted shape of a tomato worm as it easily moved around a 90° turn in the garden without changing its volume. The Aero Medical Laboratory contributed the multi-layered liner, resembling long johns, that had thousands of tiny holes to allow proper ventilation of air around the pilot's body (4).

#### *The Mercury suit*

The space suit for the Mercury program was a direct result of these early concepts for advanced techniques and materials. The astronaut donned air-cooling underwear first. The suit had a vulcanized, double-walled layer ending in integrated feet; a perforated inner wall permitted the body to cool by evaporation. The coverlayer incorporated a high-temperature resistant, aluminized nylon with fabric-fluted shoulder and knee joints for mobility. A large assortment of airtight zippers, laces, and straps aided donning and doffing. Semi-hard, high-top aluminized shoes gave the astronaut support. The helmet and gloves were fastened to the suit by airtight metal joints that rotated on sealed bearings. The helmet's hard outer shell was fiberglass with a clear Plexiglas visor. An electrical cable carried communication system wiring attached to earphones and dual adjustable microphones (5).

#### *The Gemini suit*

Mercury suits were simple backup suits in case the spacecraft lost pressurization. For Gemini missions, suits had to protect astronauts from the hazards of space walks as well. The David Clark Company, who had researched and built earlier pressure suits for experimental planes, was chosen to make suits for the Gemini program. The important breakthrough feature of these suits was linknet, a lightweight yet extremely strong network of Dacron cord woven like fishnet into interconnecting links throughout the suit (6). This linknet greatly reduced the suits' tendency to "balloon" while under pressure and, therefore, increased the astronauts' comfort and mobility.

Gemini astronauts wore cotton long johns underneath their suits. The torso consisted of an Oxford nylon liner fastened with Velcro to the gas container layer made from neoprene-coated rip-stop nylon. The liner assembly diffused ventilation gas over the entire body. Nomex linknet replaced Mercury suits' numerous straps to restrain the gas container to the contours of the body. The cover layer was fabricated from several layers of uncoated nylon over alternating Mylar and Dacron batten superinsulation, with a final layer of nylon projectile-resistant material. The helmet had a fiberglass and resin dome with a methacrylate visor. Two overvisors protected against glare, ultraviolet light and micrometeoroids. Gloves were designed for finger sensitivity, durability, and abrasion protection. Boots, attached to the suit, contained layers of nylon, cotton-covered sponge, high-temperature fabric, and a multilayer protective cover.

#### *The Apollo suit*

For Apollo, exploring the moon would require the most complicated suit yet devised (See fig. 2). Long john underwear for these astronauts contained a liquid cooling system composed of an interlacing of capillary-like PVC tubing woven

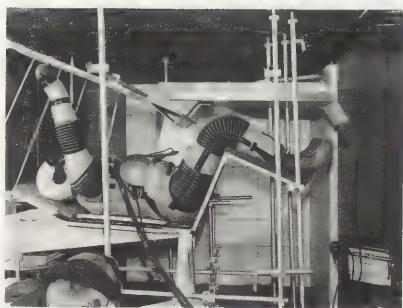


Figure 2. Apollo Work Analyzer. Reach limits of early developmental suit, pressurized to 3.5 psi. NASA photo #S-64-18287.

through nylon Spandex attached to a comfort liner of nylon tricot. Next came the integrated micrometeoroid garment. The outermost layer was super Beta cloth, created and designed by the National Aeronautics and Space Administration (NASA) scientists for specific characteristics: strength, thermal resistance, flexibility, ability to self-extinguish, and infusibility. Beta silica fiber was coated with Teflon and spun into yarn which was then woven into Super Beta cloth. Two layers of aluminized Kapton came next, integrated with Beta cloth marquisette, used as a spacer to reduce heat conduction, between Kapton layers. Five layers of aluminized Mylar spaced with nonwoven Dacron scrim followed. Kapton was found to suffer from wear and was replaced with Beta marquisette-reinforced polyimide film. The innermost layer was neoprene-coated nylon fabric. A bubble-shaped polycarbonate helmet replaced the conventional, pilot-style closed helmet. Hard boots were replaced with an all-soft construction. Gloves gave a better grip because of a coating of a slip-resistant silicon dispersion compound over the metallic Chromel-R layer covering the palm.

### Suit locations

For the Mercury program, there were seven single passenger flights of increased duration and complexity. For the Gemini program, there were 10 two-men flights that included multiple docking practice and walks-in-space. For the Apollo program, there were four three-men translunar missions, seven three-men lunar missions, three three-men Skylab missions, and one three-men Apollo-Soyuz mission. This is a total of 34 missions and 72 astronauts. Each astronaut had three suits, one for training, one for backup, and one for flight for a total of 216 suits.

Of the 216 suits, the National Air and Space Museum houses 61 mission-related suits in environmental storage. Eight flown suits are on exhibit. Eighty mission-related suits are on loan to museums around the world. There are 17 developmental suits in environmental storage and 12 developmental suits on loan to other museums.

When the suits first began to come into the collection in the 1960s and early 1970s, there were few NASM curatorial staff members. The staff members were housed in the Arts and Industries building and the artifacts were stored in available warehouses. The first exhibit area for air and space artifacts was temporary—a quonset hut once located behind the Smithsonian Institution Castle. The next facility, the Arts and Industries building, was also temporary. The first priorities before the museum opened in 1976 concerned planning and implementing the new exhibit areas. By this time, large shipments of space artifacts were coming into the Garber Facility. The loan program became the next priority because of the demand to borrow space artifacts.

In 1978, the Smithsonian called for an institution-wide inventory of its artifacts. NASM's inventory revealed damage to the collection from years of poor storage. NASM requested recommendations from Conservation Analytical Laboratory, which suggested an environmentally controlled storage area (7). Once this was installed, it was possible to sort the collection into a preservation/study collection and a collection that could be loaned.

In 1989, NASM's collection management group hired a conservator, Ed McManus. The Conservation Analytical Laboratory also added a research organic chemist, Mary T. Baker. McManus and Baker began to research and study the collection.

### Suit conditions and materials survey

A survey of the suits was conducted to identify the major types of chemical deterioration that had taken place, in order to determine if the suits were in further danger. Three areas of damage stood out: deterioration of PVC tubing, discoloration of aluminized fabric, and embrittlement and flaking, or oozing and distortion, of rubber-like components.

Polyvinyl chloride (PVC) tubing is the main working component of the liquid-coolant garments. Soft PVC is always a concern to a collections manager; it is



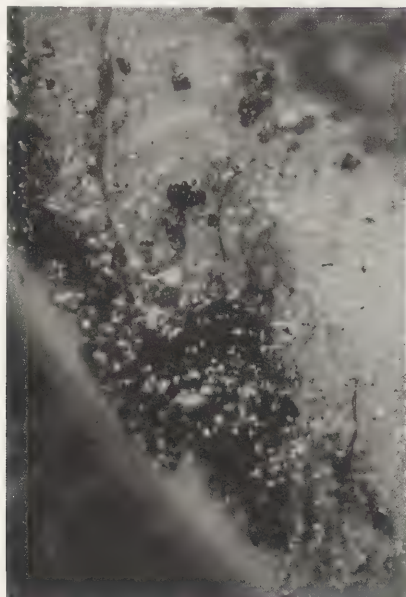


Figure 3. Photomicrograph of PVC tubing piece (magnification 200 $\times$ ). Note plasticizer droplets and accumulated dirt.

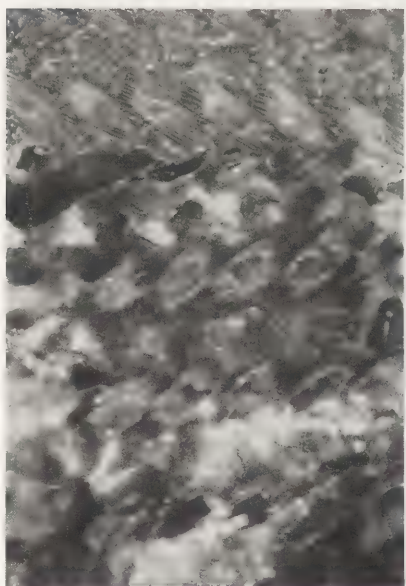


Figure 4. Photomicrograph of aluminum/adhesive fragment (magnification 200 $\times$ ). Note imprint of fabric in the orange adhesive, and the remaining specks of aluminum.

known to out-gas small amounts of hydrochloric acid (HCl), which damages metals and fabrics. Additionally, soft PVC is highly plasticized (usually with a dialkyl phthalate) in order to keep it rubbery (in contrast with the hard PVC plumbing stock, which is unplasticized). This plasticizer is not compatible with the resin and will eventually migrate to the surface, where it will attract dust and stain fabrics. This oily material also poses a threat to other plastic parts in the vicinity, as it can migrate into them and plasticize them; since many plastics are soft by nature, such extra plasticization will turn them to a sticky liquid.

A close inspection of the PVC tubing revealed that the PVC has begun to yellow and that it had a low surface pH (pH 1–3, measured with a test strip left in contact with the surface for several days), suggesting that it is deteriorating and is out-gassing in the process. Microscopic examination (magnification 200 $\times$ ) revealed dirt accretion and droplets of plasticizer on the surface (See fig. 3). The loss of plasticizer has stiffened and shrunk the tubing.

The discoloration of the aluminized fabric (which, to the naked eye, strongly resembles rust) is caused not by a change in the color of the aluminum, but by actual loss of the aluminum. Under close examination, a coating can be seen in the rust-colored areas that appears brittle; when it is flaked off, the olive fabric underneath shows through. Microscopic examination of these areas reveals that the aluminum layer is adhered to the fabric with an orange resin (See fig. 4). This resin seemed to once have been rubbery, but is now brittle, causing the aluminum to flake off and reveal the resin underneath, causing the color change. FTIR microspectroscopic analysis revealed the resin to be a nitrile rubber adhesive, which should be very stable. The manufacturers of these materials confirmed the analysis and supplied a contemporary sample of the aluminized material (8). The adhesive on that sample is still fluid and sticky, suggesting that the suits in our collection have undergone unexpected deterioration, perhaps due to exposure to unusual conditions before they were acquired by the museum.

Examination of the rubber components revealed that they, too, were brittle; however, many of them seem to have gone through a phase of stickiness and oozing before hardening. In some cases, inside surfaces of the suits were in better condition than outside surfaces, and suits which had been on missions were in better shape than unflown suits. Because the unflown suits were often used in neutral buoyancy exercises, in which the astronauts practice maneuvers in tanks of water, we suspected that the chlorinated water used in these tanks could be partially responsible for the present state of deterioration of both the rubber components and the adhesive. Tests using raw isoprene exposed to calcium hypochlorite solutions (at swimming pool concentrations) supported this line of reasoning. FTIR microspectroscopic analysis showed that, upon natural and artificial aging, the chlorine-exposed rubber oxidized far more rapidly than samples exposed to distilled water (9).

These deterioration problems cannot be reversed; they can only be slowed and monitored. Articles containing PVC must be kept separate from the other articles; low-temperature storage will slow the deterioration of the resin, but not the migration of the plasticizer. Minimizing airborne dirt will prevent the plasticizer from attracting dust; buffered storage can counteract HCl out-gassing, but the plasticizer may eventually stain the fabric portions of the garment. The present low-temperature storage of the suits has reduced by at least one quarter the degradation rate of the adhesive and rubber components; minimal handling of the suits will limit the damage to the now brittle materials.

Cold storage of these materials, while it obviously slows the degradation rates, was of concern because of the crystallization tendencies of natural and synthetic rubber. Natural rubber will crystallize to its fullest at room temperature after about 40 years, and this crystallization can only be reversed by prolonged heating for several days at 60°C or higher (10). However, the same state is reached after only a few years at 5°C, and less than a day at –20°C (10, 11). However, while the materials crystallized at 5°C would need to be exposed to 30–35°C for several days to remove the crystallinity, those exposed to –20°C would only need to be exposed to 5–10°C (11).



It is clear, then, that the suits presently in cold storage must be handled with extreme care, as they are probably at their maximum crystallinity, and that warming them to room temperature is not sufficient to decrystallize them. Since these suits are being preserved for study and not for display, the need to limit handling is not a severe drawback; indeed, the cold storage has extended the life expectancy of the suits (quadrupling their lives, at the least). However, it remains to be decided if we should lower the storage temperature even more; any rubber-containing materials we might add in the future would then be less brittle at room temperature (and the deterioration rate would drop even further).

### The emergence of a conservation/preservation plan

When spacesuits first began to enter the collection of the National Air and Space Museum, little was known about what special precautions might be required to ensure their preservation. Development of a conservation/preservation strategy was delayed by common misconceptions about modern materials and about space equipment designed to withstand the harsh environment of space. Along with deterioration caused by exhibit and storage conditions, in a few instances, holes were cut into the suits to accommodate various types of exhibit supports. Realistically, the spacesuits could not be placed on permanent exhibit without incurring damage. Conservation standards for the care of spacesuits would have to be developed and conditions would have to be monitored to ensure that the standards were being met.

One of the first actions taken was to retire those suits that were most damaged and, in some instances, to replace them with reproductions. For instance, the Gemini 4 cover layers of Ed White's and James McDivitts' suits suffered ultraviolet damage from being exhibited unprotected before the large windows of the museum; these covers were retired to storage and replaced with reproductions. In May 1992, John Glenn's Mercury spacesuit was removed from exhibit after 17 years of display. Eventually all spacesuits currently on loan will be recalled for conservation condition evaluation.

It is not known how long spacesuits can be exposed to visible light and ultraviolet radiation before being damaged. It was decided to limit exposure to 200 LUX (20 footcandles), the upper limit of the generally recognized museum standard of 50–200 LUX (5–20 footcandles). UV radiation was limited to the museum standard of less than  $75 \mu\text{WATT/Lumen}$  (12). Admittedly, these values do not take exposure time into account. Those museums with spacesuits on loan from the National Air and Space Museum are now asked to provide visible light and UV readings when renewing the loan of a spacesuit. Initially, it was discovered that very few air and space museums that had borrowed spacesuits had the equipment to take the required readings. For some, it was the first time that light level readings were taken in their exhibit area.

It is estimated that a reasonable accumulated lifetime exposure of 600,000 to 1,800,000 LUX hours may be appropriate for spacesuits. This is approximately two to four years at 100 LUX. Most exhibited spacesuits have probably exceeded this figure several times already. Further analysis is required in the form of accelerated aging of test fabric in a weatherometer in order to determine appropriate exposure time.

It is possible to evaluate light damage to those suits that have been on exhibit for extended periods. A "Minolta Chroma Meter CR-200" is now used to evaluate color shifts that have occurred to various portions of a spacesuit (See fig. 5). This instrument can be used to compare exposed surfaces with unexposed surfaces, such as those found in pocket flaps, folds, and front and back elements. The  $L^*a^*b^*$  color opposition scale expresses the color in numerical values. A degree of caution is required when using the instrument because other factors beside light damage can account for a color shift. Among these are abrasion, dirt and dust, and the aging properties of certain suit materials. Some Gemini spacesuits appear to become uniformly darker and yellower, a change that can not be attributed to light damage at this time. In most instances, however, the color shifts fit a pattern for exhibit lighting, with the greatest color shifts occurring on the front and the upper surfaces around the shoulders. With this



Figure 5. Pugi Josep Subagiyo, Conservation Analytical Laboratory Visiting Scholar, making colorimetric measurements of John Glenn's suit. Ed McManus photo.



instrument, it is possible to measure the difference between a spacesuit material that has remained in storage and the same material that has been on exhibit for an extended period. The instrument can also be used to evaluate a spacesuit going on loan or exhibit for the first time.

The National Air and Space Museum has also developed an artifact loan program package for prospective borrowers. The package contains two sections relevant to the preservation of spacesuits: "Conservation Standards" and "Guidelines for the Exhibition, Care, and Handling of Spacesuits." Among the recommendations are specifications for mannequin support.

These actions represent a marked improvement in the care of historic spacesuits, however, additional work is required. Analytical research on modern materials is extremely relevant to the development of appropriate conservation/preservation procedures. As such research progresses, NASM will be able to implement better collections care for the spacesuit collection.

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### Abstract

An outstanding Renaissance coat woven with metal threads suffered heavy deterioration due to war damages and aggressive environmental factors. During restoration, most signs of deterioration and incorrect previous restorations were eliminated. The condition of the object improved, its pieces were supported, and the original shape was retained.

### Keywords

Coat, lampas, metal threads, disassembly, cleaning, supporting, reassembly, material investigation, morphological investigation

## Restoration of a 16th-Century Child's Coat ("Mente") Belonging to the Esterházy Collection

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### Introduction

The object is an outstanding early piece from one of the Hungarian peers' collections founded by Miklós Esterházy; this collection has since become famous. According to the inscription found in the lining of the coat (called "mente" in Hungarian), Miklós Oláh (1493-1568), a renowned humanist prelate and archbishop of Esztergom, who wore it as a 10-year old boy in 1503 (1, 2).

Restoration of the coat took place on two occasions, first in 1953 and later in 1960. The acute weakening of its fabric necessitated restoration, as it became impossible to exhibit the piece without causing additional deterioration.

### Description of the object

The coat, a piece of clothing worn over the dolman, has a straight-fitting shape from shoulder to waist; from the waist down, it widens out. The length reaches to about the middle of the thigh. The sleeves are tailored in the shoulders and hang down to the lower hem.

Further inward from the seams of the sleeves are openings: the wearer of the coat could extend his arms through them. Similar construction occurs in the long-sleeved types of coat with the difference that the slits were left open in a part of the sleeves seams (3). Other slits, which appear at the waist, may have been the pocket openings, or may have been openings to access swords worn at the hip. The collar, which spreads over the shoulders, is cut of several pieces. No traces could be found to suggest a fastening at the front of the coat (See figure 1 and photos 1, 2).



Photo 1. Front view of the coat ("mente"), before restoration.

Photo 2. The back of the coat, before restoration.

Most recent researchers consider the fabric of the coat to be of Turkish origin, but concrete data are not available concerning its provenance. Judging by its design, it may be ranged with big-pattern fabrics (4). The surface of the material is divided into so-called "mandorla-form" fields by silver-gilt metallic brocaded



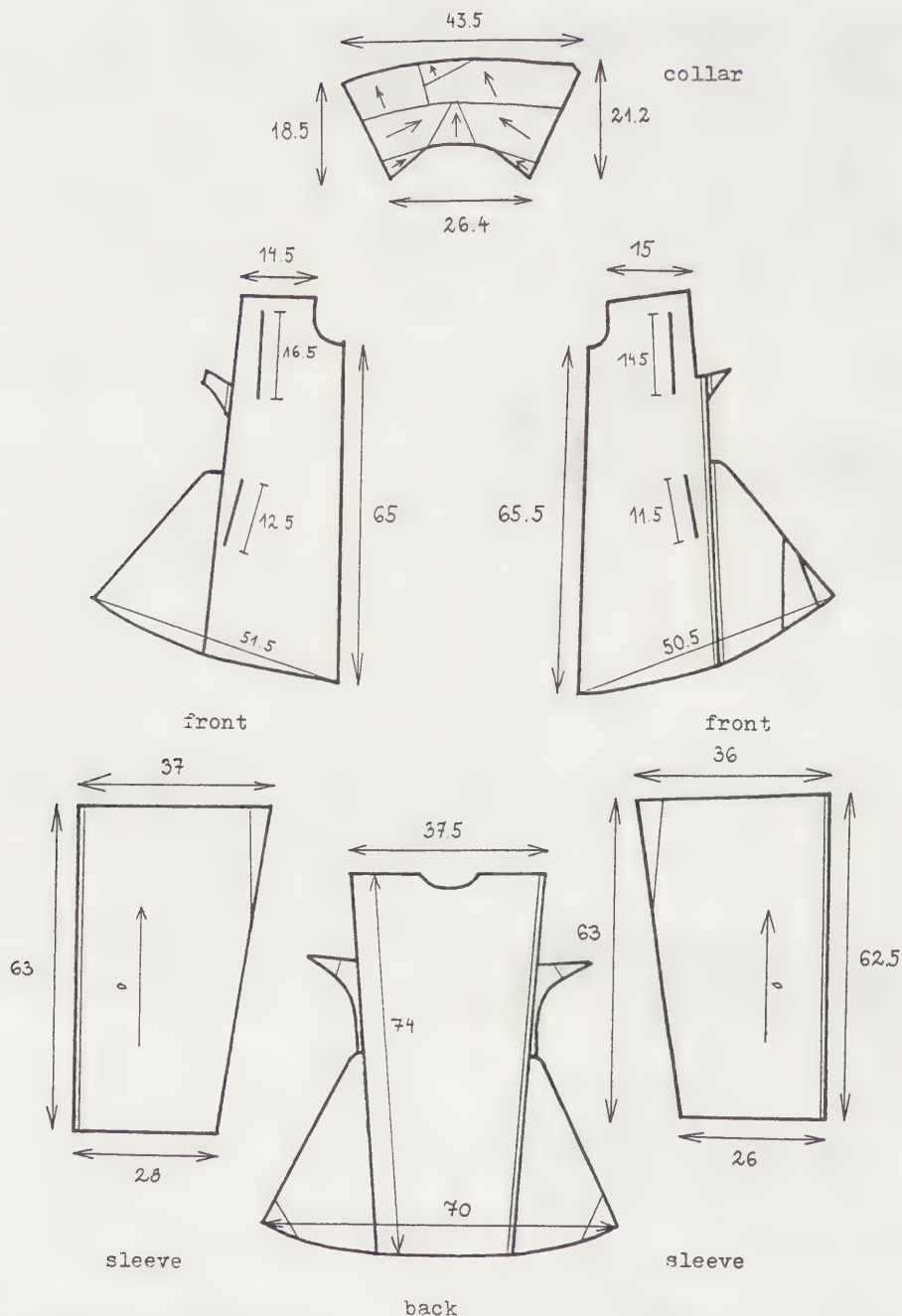


Figure 1. Pattern of the coat.

bands. The inner fields are weft-patterned, lanciert with silver yarn. The bands are decorated with five types of fantasy flowers, tendrils, out of which carnations, roses, and tulips grow (See photo 3). The fabric was probably made on a puller or Chinese loom.

### Material testing

The examination of the fibrous materials was carried out with optical microscope. In the course of testing, it was unequivocally shown that the fabric is made of silk yarn. (See Table I).

A wet analytical process was used for indigo; for the rest of the colouring matter thin layer chromatography was used (5,6). The results of dye identification are outlined in Table I. For silk, it can be inferred that indigo yarns were coloured using a vat-dye treatment; for the rest of the colours, mordants were possibly used.

The morphological examination of the metal threads was done with optical and scanning electron microscopes. The gilding was ascertained in a specially-designed microchemical test using an optical microscope; energy-dispersive mi-



Photo 3. This photograph (taken before World War II) illustrates the still undamaged state of preservation of the coat. The graceful lines in the design of its fabric are clearly discernible.



Photo 4. Pattern number 1 (the microscopic picture of the lanciering weft).

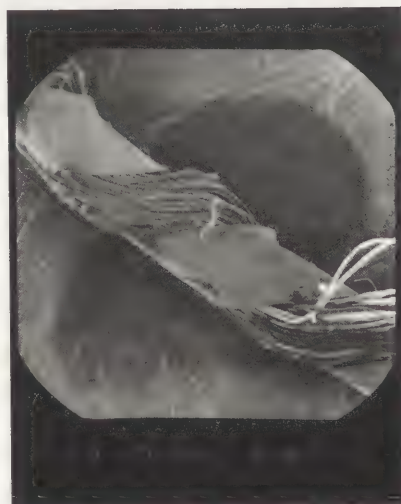


Photo 5. Pattern number 2 (the microscopic picture of the lanciering weft).

Table I. Result of material investigations.

Denomination	Lampas, Lanciered, brocaded	
Width of fabric	68 cm	
Pattern	Height: 69 cm	Width: 34 cm
Selvage	Striped, self-coloured and red 0.3 cm	
Ground	Warp: main	Weft: Ground I.
Material	Silk	Silk
Colouring matter	Colour: Red Polish Cochenil (Margarodes polonicus)	No colouring agent
Density	96/cm	26/cm
Twist	Untwisted?	Untwisted
Weave	5-ply warp-effect atlas	
Pattern	Warp: binding	Weft
Material	Silk	Lanciering weft 1. Self-coloured silk 2. Silver band twisted around self-coloured silk 3. Green silk Brocading weft 4. Silver gilt band twisted around yellow silk wick
Colouring agent	No colouring agent	3. Indigo + dyers' greenweed 4. Dyers' greenweed (Reseda l.)
Density	26/cm	24/cm
Twist	Untwisted	Untwisted?
Weave	4-ply weft-effect twill	

croanalysis was also done (7). The metal bands of the metal-wrapped threads were presumably made from flattened drawn wires. It was inferred that the silver-gilt yarns could have been produced by a similar technique. (Table II and photos 4–6)

### Condition report

We studied the history of the Esterházy collection for background information on the condition of the coat. The collection was taken over by the Museum of Applied Arts in 1919 for the first time as a deposit. Before World War II, the heir annulled the contract and had the objects transported to a new location that was later heavily damaged in a bombing raid, during which irreplaceable treasures were lost. The state of the remaining art objects deteriorated during the following four years until they were reacquired. During that time, they had been exposed to rainwater under ruins and became heavily corroded (8). The condition of the objects was affected by the environmental factors they had suffered. To some degree, the change in the fabric of the coat can also be traced back to these circumstances. Beyond the war damage, the weakening can also be attributed to the bad climatic conditions, the unsuitable lighting, and humidity, all of which were characteristic of the exhibition's environment. As a result of the combined effects of all these factors, the fabric became weakened, the metal threads corroded, and flaked off the surface (See photos 4–6). In addition, the previous restorations partly deformed the object. Considering the condition of the object, we found it imperative to supply it with a full support.

### Restoration methods

In order to facilitate the stabilization of the object, the straightening of the fibres, and the lining with the supporting material, the object had to be disassembled into pieces. First, the lining applied in the previous restoration had to be removed. After undoing the seams and the couching stitches from the former



Table II. Result of the morphological and material investigations of the metal yarns.

Pattern	Yarn thickness (mm)	Metal band			Twist	Colour of wick	Mode of production
		Material	Mode of gilding	Width (mm)			
1.	inner: 0.25 full: 0.30	Ag	—	inner: 0.25; 0.30 outer: 0.15	Z S	self-coloured	Metal band wound around wick yarn
2.	0.20	Ag	—	0.25 0.30	S	self-coloured	Metal band wound around wick yarn
3.	0.20 0.25	Au	On side 2.?	0.30	Z	yellow	Band rolled of silver gilt wire wound around wick yarn
		Ag	bad quality				



Photo 6. Pattern number 3 (the microscopic picture of the brocading weft).

restoration, the weak structure of the fabric became still more obvious, confirming the necessity of a complete support (See photos 7, 8).

Before wet cleaning, the dust on the surface was removed using a low-power, record-disc vacuum cleaner. I considered wet cleaning necessary because of the presence of some stains, which—although unimportant from museological and aesthetic aspects—were damaging. In addition, I was able to exploit the plasticising and softening effects of the water, enabling me to correct the deformations and distortions of the material.

The 0.5 g/l Hostapon T (anionic detergent) washing solution was prepared with soft water. The solution had a pH of 6–7. The washing time had to be reduced to a bare minimum, as the cleaning, in spite of all useful effects, imposed considerable stress on the object. To reduce the washing time, the excellent foaming capacity of Hostapon T was exploited. With the aid of the foam, the impurities could be removed from the surface much faster and in greater quantity; thus, the danger of stain and soil redeposition was significantly reduced (9).

First, I let the foam that was formed from the washing solution cover the object and let it stand for 10 minutes. Thereafter, I used a sponge to absorb the wash solution and impurities. These steps were repeated several times. In order to remove the residual surfactant molecules and impurities, the coat was rinsed three times; the final rinse water was clear.

To ready the wet object for drying, I laid out the various pieces according to the original form; the fabric was set and adjusted as required by the direction of the fibres and yarns. To avoid shrinking while drying, the edges of the fabric, the inner seams and the edges of the slits were fixed with thin, non-corroding entomological pins.

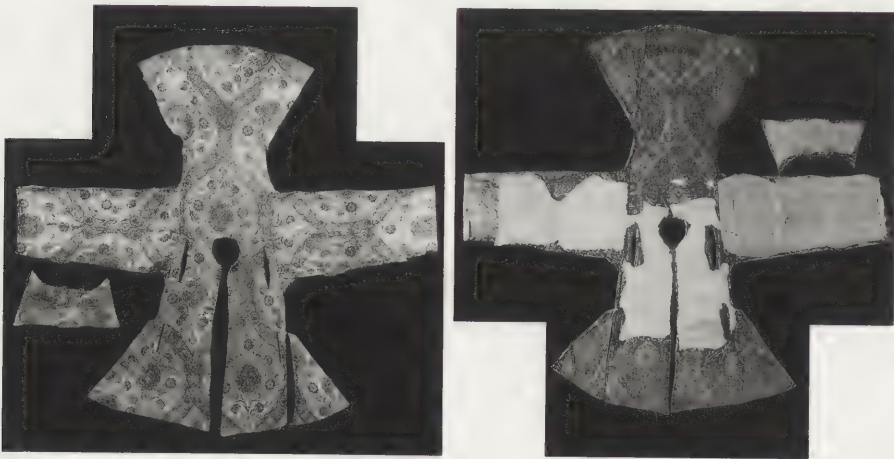


Photo 7. The coat spread out after the side seams have been removed.

Photo 8. The coat spread out after the side seams have been removed. On the inner surface of the fabric, the supporting materials (applied only where strictly necessary) are visible.





Photo 9. Part of the right side of the coat before sewn conservation treatment.

Photo 10. Part of the front (right side) of the coat after conservation.

I was able to remove a considerable amount of water from the material by laying paper wadding on the surface and pressing slightly to absorb the water. Then, I dried the pieces with cold air, until they were partially dry. As I already was familiar with the properties of the dyes, I had no reason to worry about dye bleeding problems. Air-drying completed this stage of the process.

A thin, dense cotton-linen fabric capable of carrying the weight of the object was used as a support material. After boiling the fabric to remove the sizing, I placed this undyed material under the original textile pieces. I carefully aligned the yarns of support material with those of the supported pieces.

For sewing, a yellow silk thread matching the colour of the fabric was chosen. The conservation was carried out on a table, using a curved ophthalmic needle. Couching stitches, suitable to stabilize the floating wefts, were placed at 4–6 mm intervals. Conservation was extended to seemingly undamaged places that were, in fact, in need of reinforcement (See photos 9, 10).

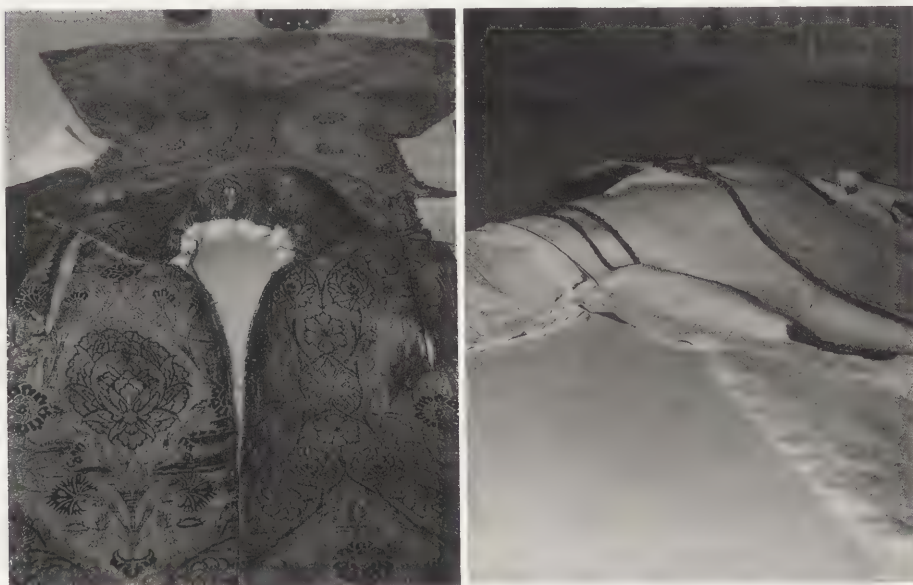


Photo 11. The pinning of the collar before sewing.

Photo 12. The coat during reassembly, with the sides pinned before sewing.





Photo 13. Front view of the coat, after restoration.

Photo 14. Back view of the coat, after restoration.

Reassembly started with sewing together the back and front parts; then, I sewed back the sleeves and the collar. By turning back the side seams, the selvages of the sleeves in the front part and in the lower hems, the coat regained its original shape. Finally, I sewed a newly-made lining into the coat (See photos 11, 12).

### Conclusions

As one result of the performed cleaning, the textile material of the coat regained its original flexibility and the metal threads become clean and bright. The fabric lined with the supporting material has become more resistant to the stresses of handling and transport, and the coat regained its original shape (See photos 13, 14). The beauty of the coat was appreciated by the visitors of a short exhibition. It is presently housed in the good environmental conditions of the store room.

### Acknowledgements

The author is indebted to Emöke László (Department Head), as well as Lilla Tompos and Emese Pásztor, art historians who carried out the research on textiles of the Esterházy collection through the financial support of the National Scientific Research Foundation.

Special thanks is also due to Katalin E. Nagy (Senior Conservator of the Museum of Applied Arts) for her generous help during each step of the work, including sharing her results and experiences.

Thanks are due to Márta Járó for carrying out the morphological and material investigations of the metal threads and to Ágnes Tímár-Balázs for identifying the dyes. The photos were made by Ágnes Kolozs and Imre Eck.

### Materials

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## Abstract

The study into the effects of conservation wet cleaning on standard, soiled wool fabric was done in order to determine the most gentle, yet efficient wet-cleaning method. The results were obtained by analysing standard soiled test fabrics from a previous series of wet cleaning tests. Comparisons were made between anionic and non-ionic detergents used in different concentrations and between different washing methods. The analyses were carried out to show changes in surface characteristics, dimensions, soil removal, tensile strength, and weight. The results demonstrated that the wool fabric shrank with each treatment. The shrinkage was more severe when the soil removal was more effective. The cleanest results were obtained with the warmest wash bath of 30°C for both detergents. This washing method was also the most damaging to the fibres. Based on the results, the use of a non-ionic detergent is recommended for the conservation wet cleaning of wool.

## Keywords

Conservation, wet cleaning, wool, shrinkage

## The Effects of Conservation Wet Cleaning on Standard Soiled Wool Fabric: Some Experimental Work

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## Introduction

It has been well recognised among conservators that wet cleaning methods and their effects in textile conservation need to be examined using analytical, objective methods in order to obtain representative results. A big problem in such research is the question of sampling. Without taking into consideration the ethical aspect of cutting historical textiles into pieces for tests, it is understood that each historical textile has aged and/or become soiled under different conditions and is, therefore, in a different state of degradation. Bearing this in mind, even if the tests are carried out in standardized and controlled conditions the results will be representative only for each individual case; generalisation is difficult. Alternatively, studies into the effects of wet cleaning can be made using unaged, standard soiled fabrics. Although the results thus gained will not be directly comparable to naturally aged and soiled textiles, which usually are considerably weaker than similar types of modern fabric, they do give some indication about the nature and scale of the effects of wet cleaning.

The aim of this study was to examine any changes in properties of woollen textiles caused by different washing methods, detergents, and washing solution concentrations. The test samples comprised unaged, standard, soiled test fabrics. The following properties were examined: surface characteristics, including colour; dimensional changes; soil removal; tensile strength; and weight. The analyses were carried out by visual examination, weave density measurements, ultraviolet-visible reflectance spectroscopy, tear-resistance testing, and weighing. The samples used in the analyses were provided by a series of conservation wet cleaning tests that had been carried out by first year students of the Post-Graduate Diploma Course in Textile Conservation at the Textile Conservation Centre (TCC) at Hampton Court in June 1991.

## Wet cleaning experiment

The series of wet cleaning tests carried out at the TCC in June 1991 were derived from the work of Eastaugh and Shashoua (1, 2). The tests in 1991 and in the present study were carried out on unaged, standard, soiled test fabrics of wool and cotton that were produced by Wascherei Forschungsinstitut Krefeld in Germany and supplied by Westlairs Ltd. (3). Two different detergents—Synperonic N, a non-ionic detergent, and Sodium dodecyl sulphate (SDS), an anionic detergent—were used in three different concentrations. Sodium carboxymethyl cellulose (CMC) was added to the washing solutions of both of the detergents. Three different washing methods were tested: mechanical action at room temperature, mechanical action at 30°C, and a five-hour soak in washing solution followed by mechanical action at room temperature.

An anionic and a non-ionic detergent were tested in order to discover whether there were any noticeable differences in their behaviour and in their effects on fibres. Anionic detergents have been considered more effective on cellulosic fibres than on protein fibres, and sometimes an anionic detergent is used at the end of a wet-cleaning treatment to flush out any remains of a non-ionic detergent used initially. On the other hand, anionic detergents have been considered more damaging to the fibres (4).

Three different concentrations of each detergent was tested in order to assess the lowest concentration needed for effective and least damaging wet-cleaning treatment. Two different temperatures were tested in order to assess the significance of the wash bath temperature and to determine if higher temperatures cause damage to the fibres.

Three different washing methods were tested in order to compare the results and to use them together with the other results to determine the most suitable washing method of those tested for conservation use.

### Test design

The wet-cleaning tests were carried out on two different fabrics, wool and cotton. Only the wool samples were analysed further in this study. The wool fabric was plain-woven and undyed. Its natural colour was yellowish white; it appeared grey when soiled with the standard soils that had been sprayed on one side of the fabric only.

The test fabrics were categorised as follows:

*Fabric A: Wool/Olive oil*

Plain-woven wool fabric soiled with a special soiling composition (olive oil and other components) designed for wool.

*Fabric B: Wool/Sebum BEY*

Plain-woven wool fabric soiled with WFK Standard soil (86% china clay, 4% black iron oxide, 2% yellow iron oxide, 8% organic red pigment) and 1.5% synthetic sebum (Sebum BEY).

Each washing solution was formulated using 0.5 mg CMC in 1 litre of softened water combined with the following dosages of Synperonic N: for the non-ionic detergent solutions, 0.1 ml, 0.2 ml, and 0.4 ml; and for the anionic detergent solutions, 0.1 ml, 0.3 ml, and 0.6 ml.

The samples, measuring approximately 120 × 170 mm, were weighed prior to wet cleaning. The pH of the wash bath was recorded and the samples were left to soak for five minutes. The samples undergoing mechanical action treatment were sponged on the front and back following a regular pattern for ten minutes. Then the pH of the wash bath was recorded. A second wash bath was given with the same amount of sponging, and then the pH of the wash bath was again recorded. The samples were rinsed with softened water in four flood baths of five minutes each. The final flood rinse was done with deionised water. The samples were blotted in cloth, pinned out to shape, and dried with a dehumidifier. The samples undergoing both soaking and mechanical action treatments were first left to soak for five hours in the wash bath, then treated with the mechanical action described previously. Finally, all the samples were weighed. Total times for the wet treatments were approximately one hour and six hours, respectively.

### Research design

The test fabrics were selected for the following reasons: The test was systematically structured and executed under controlled conditions. The samples were comparable with each other because of the homogeneous quality of the test fabrics. The fabrics provided a potential source of information capable of being analysed systematically.

After wet cleaning, the samples were examined for changes in surface characteristics, dimensions, tearing resistance, and weight. Also, the relative rate of soil removal was examined. The analysis methods chosen were visual and microscopic examination (with a stereo-microscope), weave density measurements, tensile strength testing, weighing, and ultra-violet-reflectance spectroscopy. The analysis methods were chosen in consultation with Yvonne Shashoua, who used similar methods in her study on the effects of aqueous immersions on textiles (2).

### Changes in surface characteristics

The wet-cleaned samples were examined with and without magnification. A Baush & Lomb stereomicroscope was used for the more detailed examination with magnifications ranging from 40x to 70x. During the visual examination, the samples were compared to unwashed controls in order to detect any changes in colour and in surface characteristics of the fabric.



In this paper, the term "colour" refers to the colour caused by the evenly sprayed soils, which appeared grey on the samples.

The samples that appeared through visual examination to be the cleanest were noted. On Fabric A samples, the best results were obtained with 0.4% Synperonic N + CMC at 30°C and with 0.4% Synperonic N + CMC at room temperature with a five-hour pre-soak. On Fabric B samples, the best results were obtained with 0.2% Synperonic N + CMC at room temperature, the same solution at 30°C, and the same solution, again, at room temperature with a five-hour pre-soak.

When the colours of the samples were compared to each other after treatment, it was noted that the samples of Fabric B had become clearly less grey than the samples of Fabric A. This can be explained by the different composition of the soils; the WFK Standard soil with synthetic sebum is easier to remove by the detergents tested.

The samples were examined on both sides with a stereomicroscope to make observations about soil particles and fibre condition. It was noted generally that the washed samples had less soil particles than the unwashed controls, which was to be expected. The remaining soil was found to comprise finer soil particles and was trapped deeper between the fibres. The soil particles had remained on the front of the samples where the soil had originally been sprayed on; the soil particles had not washed through to the reverse. On some of the samples, particles of clear residue were detected. This is difficult to explain except as a possible residue of the washing solutions. The residue was more often observed on samples washed with the anionic detergent (13 of 18 samples) than on those washed with the non-ionic detergent (6 of 18 samples).

When the surface of the samples was examined, it could be seen that the weave in all of them had become tighter, which was expected because of the shrinkage of wool in aqueous treatments (6). The visual examination did not reveal any obvious changes in the fibre condition, such as breakage, roughness, or twisting.

### Dimensional changes

Weave density measurements were taken from each sample. The number of warps and wefts was counted over 10 mm. To obtain statistically representative results, this process was repeated five times on each sample and then the arithmetical mean calculated. The mean values of the wet-cleaned samples were compared to those of the soiled, unwashed controls. Comparisons of the mean values were made between different washing methods, different washing solution concentrations, and different detergents. The statistical significance of the dimensional changes was tested at the 95% confidence level and was found to be significant in all of the cases except for 0.2% Synperonic N + CMC and 0.1% SDS + CMC used on Fabric A. Generally, the warp threads shrank more than weft threads.

When the dimensional changes caused by the three washing methods were compared to each other, it could be concluded that the biggest percentage of shrinkage occurred on the samples washed with mechanical action at 30°C. The smallest percentage of shrinkage was observed on the samples washed with mechanical action at room temperature. The same results were obtained on both Fabric A and B.

Among the samples washed with Synperonic N + CMC, the biggest percentage of shrinkage occurred with the washing solution concentrations of 0.1% and 0.4% on Fabric A, and with the washing solution concentration of 0.2% on Fabric B. Generally, Fabric B samples underwent a greater change in weave density than the samples of Fabric A.

Among the samples washed with SDS + CMC, the biggest percentage of shrinkage occurred with the washing solution concentration of 0.6% on Fabric A, and with the washing solution concentration of 0.3% on Fabric B. Also, the samples of Fabric B shrank more than the samples of Fabric A.

No significant difference could be detected between the total means of the percentage of shrinkage caused by the two different detergents.

### Removal of soiling

In order to determine the relative rate of soil removal by each washing method, the ultraviolet reflectance spectrum of each sample was measured by using a Perkin-Elmer 551S ultraviolet-visible spectrophotometer with an integrating sphere attachment (7). The percentage of reflectance values at 10-nm intervals up to 760 nm were inserted into a computer program which then calculated the CIELAB colour coordinates for the following values:

L: lightness

a: redness when positive; greenness when negative

b: yellowness when positive; blueness when negative

Using these values, the colour of each test sample was compared to the colour of the soiled, unwashed controls. Diagrams 1 and 2 show the colour difference values thus obtained.

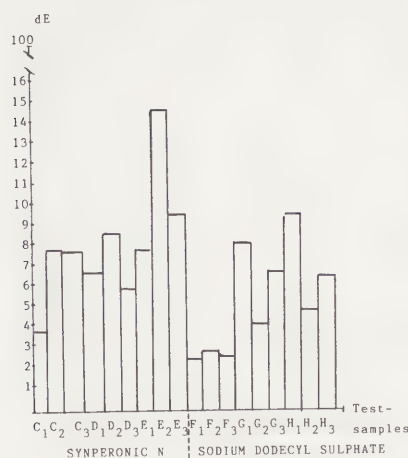
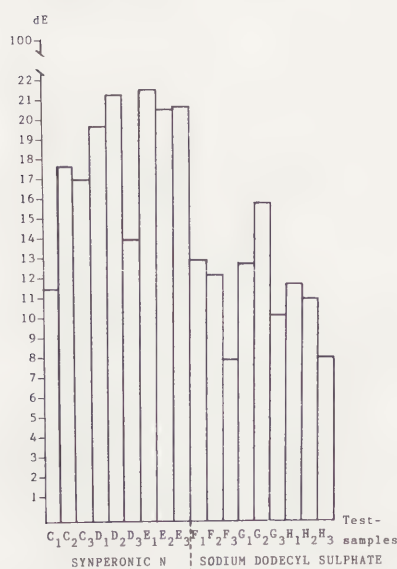


Diagram 1. Colour difference values for Fabric A, compared to soiled, unwashed Control A.



KEY: dE = Colour difference value, calculated from the CIELAB co-ordinates.  
 X<sub>1</sub> = Mechanical action at room temperature.  
 X<sub>2</sub> = Mechanical action at 30°C.  
 X<sub>3</sub> = 5-hour soak + mechanical action at room temperature.  
 C = 0.1%  
 D = 0.2%  
 E = 0.4%  
 F = 0.1%  
 G = 0.3%  
 H = 0.6%  
 } Synperonic N + CMC  
 } Sodium dodecyl sulphate + CMC

Diagram 2. Colour difference values for Fabric B, compared to soiled, unwashed Control B.

In Diagram 1, the colour difference values for Fabric A samples are compared to Control A (soiled, unwashed) samples. The diagram clearly shows that the soil removal (the change in colour when colour was caused by the soils) was generally more effective with the non-ionic detergent, Synperonic N + CMC. Synperonic N + CMC performed the greatest soil removal with mechanical action at 30°C. The five-hour soak before washing with mechanical action seemed to achieve better soil removal than just washing with mechanical action. The washing power seemed to increase as the concentration of the washing solution increased. The anionic detergent, Sodium dodecyl sulphate + CMC, gave the best soil removal action at room temperature, and the second best with a five-hour soak before washing. The anionic detergent's cleaning power also increased when the washing solution concentration increased.

Diagram 2 shows the colour difference values for Fabric B samples compared to Control B (soiled, unwashed) samples. From these results, it can be concluded that the soil removal was more effective with Synperonic N + CMC, which was also the case with Fabric A. Synperonic N + CMC performed the best soil removal with mechanical action at 30°C, followed by washing with a five-hour soak before mechanical action. The differences between the results of the different washing methods were not found to be as obvious as with the Fabric A samples. SDS + CMC seemed to give the best washing power with mechanical action at 30°C, and at room temperature. The five-hour soaking did not seem to increase the soil removal.

The results on tests of both fabrics indicate that more effective soil removal was achieved with the non-ionic detergent. These results also confirm the earlier observation (made by visual examination) that both of the detergents were more effective on Fabric B.

When the colour difference values of all the samples were compared according to the washing solution concentration, it was noted that with the non-ionic detergent the rate of soil removal increased when the concentration increased. With the anionic detergent the rate of soil removal did not increase above the concentration of 0.3%.

### Tearing resistance

The definition of the tearing resistance is given by Shashoua: "The maximum tearing resistance is defined as the highest local peak force developed when a tear is prolonged under the condition of the test" (8).

In order to detect any changes in the tensile properties of wool fibres caused by the various wet-cleaning methods, the tearing resistance of the wet-cleaned samples was tested. In preparation for the test, 20 × 80 mm strips of unsoiled fabric, soiled fabric, and soiled and washed fabric were pre-conditioned at 65% relative humidity and 20°C for four hours. A 3-mm cut across the warps was



made halfway down the longest edge, the sample was clamped into a JJ Lloyd Tensile Tester, and a load applied until the tear extended across the width of the fabric (9). Three strips of each sample were tested in the direction of warp.

From the results of the tearing resistance tests, it could be noted that no significant weakening in the tensile properties of the fibres occurred during the wet-cleaning treatments.

### Weight difference

When the initial wet-cleaning tests were carried out, the samples were weighed before and after treatments. A note was made in the results that the weight measured after wet cleaning was affected not only by soil removal and fibre loss, but also by thread loss from the raw edges of the samples. Therefore, a second attempt was made to determine the change in weight. Pieces of cloth measuring 20 × 40 mm size were cut from the samples and weighed on a Sartorius analytical balance (10). The results were compared to the soiled, unwashed controls in order to define the relative amount of soil removal.

The pieces of wet-cleaned samples were heavier than the unwashed controls of the same size. This can be explained by the fact that the fabric had shrunk during the wet-cleaning treatments and, consequently, there were more threads on the same surface area than before wet cleaning.

### Conclusion

This study was carried out to identify some of the variables in textile wet cleaning and to determine their effects. Several wet-cleaning methods, detergents, and washing solution concentrations were compared and their effects analysed. Modern, standard, soiled woolen test fabrics were used for the initial wet-cleaning tests.

In general, the results of wet cleaning appeared rather poor; the samples, particularly those of Fabric A, remained grey or greyish after wet cleaning. The soil on Fabric A was partially composed of olive oil and oily soils are known to be difficult to break down; to obtain successful soil removal, oily soils require more alkaline conditions than were provided (11, 12). On the other hand, wool fibres cannot withstand alkaline conditions, but are subjected to degradation. This is a serious dilemma in conservation wet cleaning as the best cleaning results are usually gained at pH 10 or more.

The results showed greater shrinkage of the fibres when the temperature of the wash bath was increased to 30°C and when the fibres were subjected to prolonged wetting with a five-hour soak. Samples of Fabric A did not shrink quite as much as samples of Fabric B. This observation could be related to the fact that the soil on Fabric A included olive oil, which might have acted as a protective shield against mechanical damage. The washing methods that produced the cleanest samples also caused the greatest shrinkage of the fibres. Of all the washing methods tested, the following ones were considered to be the safest and yet powerful enough for conservation purposes:

*Fabric A:* 0.2% Synperonic N + CMC, mechanical action at room temperature.

*Fabric B:* 0.1% Synperonic N + CMC, mechanical action at room temperature.

When the effects of the two detergents were compared, Synperonic N was considered more suitable for wool. The samples washed with Synperonic N did not shrink as much as those washed with SDS. The use of Synperonic N yielded better soil removal on both types of soil and it did not seem to leave as much residue on the samples as did SDS.

In order to gain further information about the various effects of wet cleaning on fibres, similar studies could be conducted on naturally aged fabrics and by changing variables such as pH.

### Acknowledgements

I want to thank Janey M. Cronyn, Head of Studies at The Textile Conservation Centre, for her guidance and help during my study project. A special thanks is given to S. Bradley and Y. Shashoua at the Conservation Research Laboratory, British Museum, for their help in planning the analysing methods and for the use of analytical equipment.

This paper is based on a final year project submitted in partial fulfilment of the Post-Graduate Diploma in Textile Conservation awarded by the Courtauld Institute of Art, University of London.

### Materials

Standard soiled test fabric. Produced by Washerei Forshungsinstitut Krefeld (WFK), Germany. Supplied by Westlairs Ltd., North Green, The Green, Datched, Slough SL3 9JH, United Kingdom.

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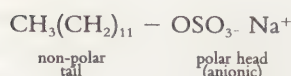


## Abstract

An examination of samples of modern silk cleaned according to textile conservation specifications revealed a residue on the sample washed with the anionic surfactant, sodium lauryl sulfate. Analysis determined that the surfactant could reach 2.73% of the weight of the fabric. Comparisons of subsequent modern silk samples revealed such residue did not radically affect the working properties of the silk, but certain differences were noted.

## Keywords

Anionic surfactant, nonionic surfactant, dry cleaning, silk, adsorption



Molecular weight: 288

Critical micelle concentration:

0.01 mole/l

Figure 1. Chemical constitution of sodium lauryl sulfate (sodium dodecyl sulfate).

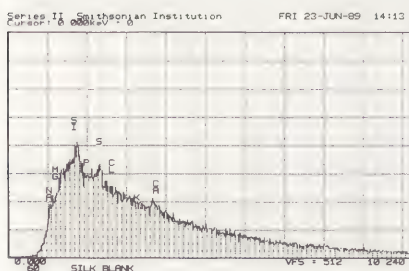


Figure 2. Energy dispersive X-ray spectrum of silk which was de-gummed with a nonionic surfactant, but otherwise untreated.

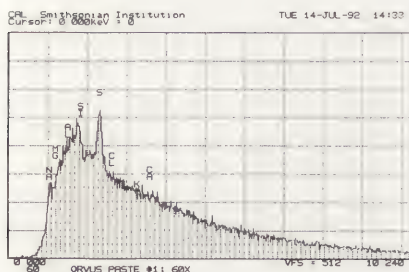


Figure 3. Energy dispersive X-ray spectrum of silk which was de-gummed with a nonionic surfactant, washed, and rinsed with sodium lauryl sulfate.

## Residues of Surfactant on Silk

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## Introduction

The cleaning of antique textiles, especially silk, has long been a concern of textile conservators (1, 3). Numerous excellent studies have reviewed the different types of cleaning agents, auxiliaries, methods of cleaning, and formulations (2,4-7). The current research focuses on the residues which have been found on silk washed with an anionic surfactant, sodium lauryl sulfate (See fig. 1) (8).

Linear alkyl sulfates such as sodium lauryl sulfate are biodegradable and incorporated into the commercial shampoos and cleaning gels for hair throughout the world. Such anionic surfactants are widely utilized for wet cleaning modern fabrics because of their ability to emulsify fatty soil. In North America, sodium lauryl sulfate, buffered to a pH 7, is widely used in wetcleaning antique textiles (5-7,9).

Physical and chemical studies indicate, however, that protein fibers adsorb anionic surfactant due to the chemical attraction between the positive sites of the protein and negative charge of the surfactant (10-14). Silk, itself, contains only a trace amount of sulfur (very minor methionine or cysteine amino acids) so elemental analysis with scanning electron microscopy energy dispersive x-ray spectroscopy (SEM-EDS) provided a qualitative means of determining the presence of surfactant residue in a silk sample. An initial comparison of a silk blank degummed with nonionic surfactant, and another silk blank wet cleaned with sodium lauryl sulfate revealed a distinct level of sulfur adsorption on the silk (See figs. 2, 3). How much surfactant is actually adsorbed by the silk and what effect the surfactant residue has upon the silk are important issues for practicing conservators.

## Sample preparation

Degummed silk fabric (Japanese habutae, 37.6 denier warp, 32.1 denier weft, 1.11 oz/yd<sup>2</sup>) was purchased from Testfabrics, Inc. The sodium lauryl sulfate buffered to a pH 7 was obtained in two forms: a paste and as a liquid (with 20% ethanol). Tradenamed Orvus, the surfactants were purchased from Conservation Materials, Ltd. The samples were wetcleaned with the method previously described by Wentz (15). A shaker bath, set at 40 cycles per minutes, was used to simulate delicate handwashing. The surfactant concentration was 0.25% v/v and maintained at room temperature for two hours. The liquid to fabric ratio was 40:1. Each sample was approximately 13 × 13 cm (5 × 5 inches).

The samples were divided into four groups for rinsing so that temperature and duration could be varied. Two rinsing temperatures (20 and 50°C) and two rinsing times (10 and 60 seconds) were used. Each sample was rinsed three times: for the first rinse, 125 ml of deionized water was used; for the next two rinses, 100 ml each rinse was used. After each washing and rinsing, the fabric and liquid sample were saved to determine the amount of surfactant remaining. The liquid samples were directly quantified by the colorimetric method.

## Analytical methods

The most well known method for measuring anionic surfactant is the methylene blue colorimetric method. In this technique, methylene blue reacts with the

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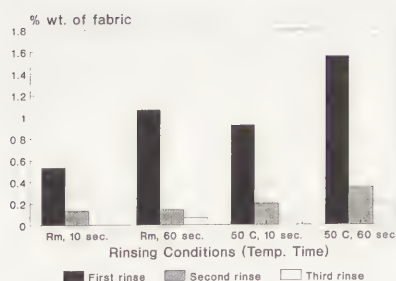


Figure 4. The amount of sodium lauryl sulfate removed by rinsing from silk treated with the anionic surfactant. The amount is listed as a percentage of the weight of the degummed fabric.

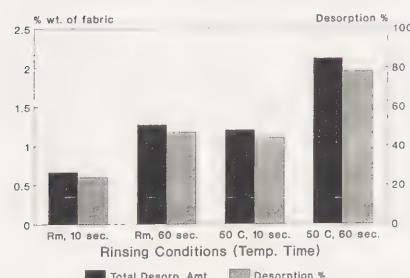


Figure 5. The total amount of sodium lauryl sulfate removed (by rinsing) from silk treated with the anionic surfactant. The total amount is listed as a percentage of the weight of the degummed fabric on the left, and as percentage of the total amount of surfactant in the fabric, on the right.

Sample	Wicking Time (sec)	Rate (cm/√sec)
Control	196.5 ± 33	0.373
3 Times Rinsed	208.4 ± 7	0.373
0.25% Treated	220.4 ± 25	0.350

a: Time to reach 5 cm

Washburn Equation:  
Wicking Distance = Rate × √time

Figure 6. The effect of sodium lauryl sulfate on the vertical wicking of silk.

Sample	Tensile Strength (Lb force)
Control	35.0 ± 5.3
Perc	42.6 ± 5.1
Stoddard	37.0 ± 2.1
Tri*	39.5 ± 2.8
Orvus	39.0 ± 4.0
Triton	42.0 ± 0.5

\* Tri: Trichloroethane

Figure 7. The tensile strength of silk treated with various cleaning agents.

surfactant and makes the colored salt which will dissolve in chloroform. The colored solvent can be measured with a solution spectrophotometer at 652 nm and calibration curves can be prepared according to Beer's Law. Beer's Law describes the relationship of absorbance to concentration of colored solutions. For systems which follow Beer's Law, straight lines are obtained by plotting absorbance, at a specified wavelength, as a function of concentration. The calibration plots can be used to determine concentrations of unknown solutions (16,17).

Since vertical wicking rates indicate surface characteristics of fibers, as described by Washburn's theory, a vertical wicking test was carried out on the samples. Vertical wicking refers to the liquid flow through a fabric in the direction parallel to the plane of the fabric. The distance traveled by the liquid is directly proportional to the square root of time. A hydrophilic fiber will have a faster wicking rate, a hydrophobic fiber surface, a slower rate. A timer was used to measure a total of 12 treated samples measuring  $1.5 \times 7$  cm, six with the longer direction parallel to the warp, and six with weftwise length. Each was marked at 0.5 cm intervals with a pencil. Each strip was lowered to just touch the water reservoir at which point the timer was started (18–20).

A variety of treated silk samples, including three treated with sodium lauryl sulfate, were subjected to tensile testing and subsequently to light ageing and color measurement. Tensile testing was carried out with a Scott Tester (Scott Testers, Inc.) at 65% RH and 20°C (standard textile testing conditions). Initially, there was no difference visually among the samples. The samples were subjected to accelerated light ageing to determine whether any color difference could be attributed to the surfactant selection through time. An Atlas-Electric Weatherometer ci-65 was calibrated and operated according to the Test Method 16-E.1990 (American Association of Textile Chemists and Colorists). That is, the chamber's Xenon arc lamp was calibrated at 420 nm for 85 kJ, with a borosilicate inner filter and soda lime outer filter. The test method was slightly modified to lower the test chamber temperature to 35°C and to maintain the relative humidity at 36–40%. Color measurements were made with a LabScan II spectrophotometer, using the C.I.E.  $L^*a^*b^*$  formulae to determine color change, delta E.

## Results

The adsorption amount of sodium lauryl sulfate on silk was determined to be  $2.73\% \pm 0.3\%$  on weight of fabric prior to rinsing. The amount of sodium lauryl sulfate that is desorbed from the silk by rinsing varies. From 75% to 80% of the adsorbed surfactant is desorbed on the first rinse. As the duration of rinsing increases, so does the desorption. With an increase of temperature, the desorption amount increases as well (See fig. 4). Total desorption, the total amount removed as a result of all three rinses, was also plotted and normalized to a percentage (See fig. 5). Here, room temperature rinsing for ten seconds removed 0.668% o.w.f. or less than 25% of the adsorbed amount. However, by increasing the rinse water to 50°C and by increasing the duration to sixty seconds, 78% of the adsorbed amount was removed.

In terms of wicking, there is not very much difference between the control and the well rinsed sample (See fig 6). However, the original absorbed, unrinsed sample (with 2.73% o.w.f.) has a rate that is significantly lower than either the control or the rinsed sample. The surface of the fabric has increased its hydrophobic character with an increase of adsorbed surfactant.

In order to compare these results with other types of cleaning, tensile testing and color measurement after light ageing were both reviewed. No significant difference was found in tensile strength among cleaned, well rinsed silk samples (See fig 7). A small but significant color difference was found among the silk samples after light ageing, particularly the longer the light exposure (See fig. 8). The dryside spotting agent, trichloroethane, had the lowest color change, along with the other chlorinated hydrocarbon, perchloroethylene. The anionic surfactant sodium lauryl sulfate produced a greater color change than that associated with a nonionic surfactant (Triton X 100, nonylphenyl ethoxalate) but less than that seen with Stoddard solvent.



Delta E, CIE L\*a\*b\*

SAMPLE	L5	L6	L7
PERC	2.31	3.76	5.12
Tri*	1.72	3.97	4.55
Stoddard	2.44	3.77	6.07
Orvus	2.48	3.92	5.79
Triton	2.51	3.94	5.20
Levak	2.94	3.31	6.04

\* Tri: Trichloroethane

Figure 8. The color difference of light aged silk treated with various cleaning agents prior to ageing.

## Conclusion

There is a possibility of surfactant residue on silk when an anionic surfactant such as sodium lauryl sulfate is used in wet cleaning. The residue amount will decrease as the temperature and duration of the water rinsing increase. However, a residue of anionic surfactant will not significantly affect tensile strength. There are, nevertheless, noticeable color differences among light aged silk samples: wet cleaned silk shows greater color change than silk drycleaned with chlorinated hydrocarbons.

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## Abstract

The relationship between effective stain removal methods and preservation of the degraded fibers underneath harmful stains is discussed. Some typical stains on historical textiles such as starch, iron and copper corrosion, and acid and alkaline perspiration were produced artificially on wool, silk, and cotton textiles and aged. Thirteen stain removal methods were applied. Colour change and whiteness of the fabrics as well as tensile strength of the fibers were measured.

## Keywords

Stain, stain removal, colour change, whiteness, tensile strength

## Effect of Stains and Stain Removal on Historical Textiles

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## Introduction

Some stains on textiles can be considered to be documentation of the function, use, and history of the object and should be preserved on the fabric. Other stains on historical textiles belong to the category of "accidental" and their removal is not questionable from an ethical point of view.

Before making decisions on stain removal, investigation of the stain as well as the condition of the fibers underneath is needed. Not only the materials but also the aged condition of the stain must be considered. When selecting solvents, solvent mixtures, solutions, and methods for stain removal, it is just as important to estimate the sensitivity of the fabric to various solutions as it is to estimate the removability of the stain.

## Harmful stains on historical textiles

Apart from ethical questions, the harmfulness of stains to fibers must be also determined when making decisions on their preservation or removal. Many stains may have a deteriorating effect on textile fibers. These type of stains include the following: solid stains that cause tension and mechanical damages by friction between yarns of woven materials; carbon black, natural dust, and other solid particles on the surface of fibers which attract deterioration agents from the atmosphere; stains containing metal ions (iron, copper, manganese, lead, tin, silver, etc.) which have a catalytic effect on photodeterioration of fibers; earthy materials and corrosion products that can cause alkaline or acid pH in moist conditions; and stains that carry out deterioration of fibers by various chemical reactions.

Deterioration products of fibers, with their dark yellowish brown colour, are not only discolouring but usually also acidic. Water stains are usually collections of acidic deterioration products that can cause acid hydrolysis to the fibers. Stains of aged finishes may cause physical damage to the textile by their hardness. They may discolour the material and their deterioration products are also often acidic, causing hydrolytical degradation to fibers. Due to their hydrophobic character, they often prevent the textile from wetting and cleaning. Fats, oils, greasy materials may embed various other dirt and can be acidic. Oily stains, containing unsaturated double bonds, may oxidize and form hard "network" stains that cause shearing stress at the edges of the stain. Oils also may age by releasing acidic products which may harm cellulose fibers.

Protein dirt such as blood, casein, egg yolk, and egg white may oxidize, forming hard, rigid stains, and may also crosslink with protein fibers. Coloured organic substances such as dyes, inks, pigments, and coloured products of chemical and microbiological deterioration of the fibers are not only unaesthetic, but they make the textile sensitive to light as well.

Microorganisms of mildew, moulds, and fungi are biological deteriorating agents that may cause degradation of fibers by their enzymatic action. They are often discolouring and the products of their metabolism is usually acidic. Adhesives on textiles may become sticky on aging or in high temperatures and thereby

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pick up various dirt. Other adhesives including animal and vegetable glues, and natural and synthetic resins may become rigid, hard, even brittle materials on aging, causing mechanical damage to textiles. Also, the pH of adhesives may turn acidic on aging.

Taking into consideration the deteriorating effect of the above listed stains on historical fabrics, restorers usually expect the condition of the fibers underneath stains and at the edges of solid stains to be in a much more deteriorated condition than in other parts of the textile.

### Methods for stain removal

Considering the above statement, it is surprising how many solvents and solutions of chemicals, those that would even damage fibers in good condition, have been recommended for stain removal. Recipes in books or articles on commercial cleaning and stain removal methods usually consider the sensitivity of various fibers to stain removal solutions, but rarely with such concern to the long-term as textile conservators should do (1, 2).

Rice provides a very detailed list on common soils and stains on historic textiles, listing some aggressive agents for dirt removal without giving concentrations of solutions, giving too much freedom to the conservators attempting to use his recipe (3). He provides a practical pH guide in which he permits application of pH 4–10 as a range usually safe for treating most fabrics, a range that has been considerably revised in recent decades. Textile conservators claim that even distilled water at pH 7 may cause hydrolysis to degraded fibers.

In conservation literature, recipes for stain removal seem to focus more on the solubility and removability of stain, than the sensitivity of the fibers underneath. "Historical" recipes for stain removal seem to survive centuries without any respect to results of recent research on fiber degradation. One must be surprised to discover in the answers to the Stain Removal Questionnaire circulated by Cruickshank and Morgan in 1991 recipes for stain removal from the 19th and the beginning of the 20th centuries (4, 5). A "reagent" such as "onion juice + hot water" for removing mold stain from cotton/linen fabric is not only "traditional," but may be damaging to degraded fibers. Also, the expression of "bleach" among the answers of the questionnaire is a term which needs further definition. Conservators should be afraid to use two of the solutions—20% solution of hydrofluoric acid and hot steam—that were cited in the survey as currently being applied in some textile conservation workshops.

Taking into consideration the deteriorated condition of the fabric underneath most stains, no stain removal can be completely harmless. In the research reported in this paper, an attempt has been made to compare the damages caused by some stain removal agents.

### Experiments

The aim of our experiments was to control the effectiveness and to follow the degrading effect of certain stain removal solutions on cotton, silk, and wool fabrics. The course consisted of four parts: artificial production of stains on the sample fabrics; aging of the samples; application of various stain removal agents; and measurement, in order to compare colour change/whiteness of the textile and tensile strength of the fibers before and after stain removal.

#### *Staining of wool, silk, and cotton textiles*

Pieces of wool (A), silk (B), and cotton (C) textiles (30 × 15 cm) were treated with various staining materials. The fineness of the yarns (almost equal warp and weft) were 142.0 tex for wool, 4.0 tex for silk, and 12.0 tex for cotton. Starch stain was produced by soaking the textile in a 100 g/l solution of wheat starch for 30 minutes. Copper corrosion stain was produced by soaking the textile in 2% solution of copper sulphate for 30 minutes. Iron corrosion stain was achieved by wrapping iron plates into the wet textile, which was kept wet for seven days. Acid and alkaline perspiration stains were produced by soaking the textile in the following solution (6):

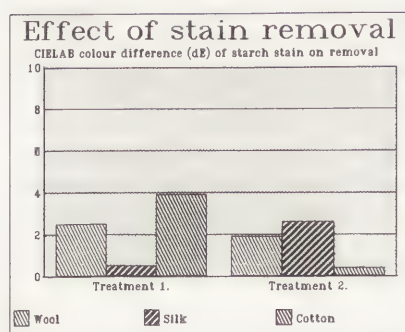


Fig.1. CIELAB colour difference (ΔE) of starch stain on removal

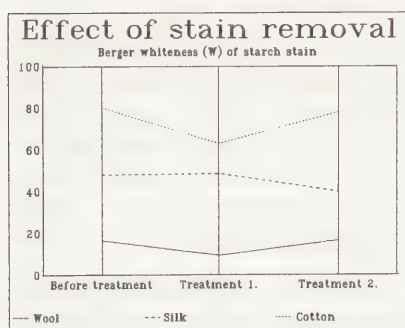


Fig.2. Berger whiteness of starch stain before and after removal

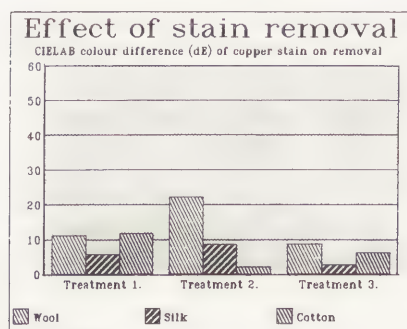


Fig.3. CIELAB colour difference (ΔE) of copper stain on removal

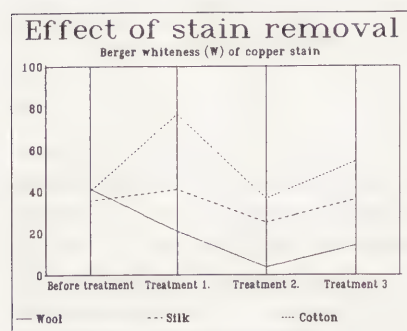


Fig.4. Berger whiteness of copper stain before and after removal

#### For acid perspiration stain:

0.5 g L-histidinium mono-hydrochloride ( $C_6H_9O_2 \cdot HCl + H_2O$ )  
5.0 g sodium chloride (NaCl)  
2.2 g Disodium-hydrogen-phosphate ( $Na_2HPO_4 \cdot 12H_2O$ )

The pH of the solution was adjusted to 5.5 by adding 0.1M sodium hydroxide (NaOH) solution.

#### For alkaline perspiration stain:

0.5 g L-histidinium mono-hydrochloride ( $C_6H_9O_2 \cdot HCl + H_2O$ )  
5.0 g sodium chloride (NaCl)  
5.0 g Disodium-hydrogen-phosphate ( $Na_2HPO_4 \cdot 12H_2O$ )

The pH of the solution was adjusted to 8.0 by adding 0.1M sodium hydroxide (NaOH) solution.

#### Aging of the stains

The aim of the artificial aging of the stains before removal was to imitate aged stains on the textiles. The aging was carried out in a Q.W. Accelerated Weathering Tester (Q-Panel Co.) with a UV-351 lamp at 60% relative humidity, 55°C temperature, for 50 hours.

#### Removal of the stains

Stains were removed by placing the textile on top of absorption material and swabbing the stains. Stain removal methods were selected from the those that were "theoretically mildest" to the most aggressive. The treatments were carried out at ambient temperature for various lengths of time, imitating common stain removal treatment. Treatment was stopped at the point where no further aesthetic improvement of the stained textile could be noticed.

Table 1. Artificial stains and stain removal methods on wool, silk and cotton.

Stain	Treatment no. and stain removal agent	pH	Duration of treatment
Starch	T1 N-methyl-2-pyrrolidone [7]	7.0	60 minutes
	T2 Diatase enzyme (0.5%)		60 minutes
Copper	T1 EDTA (5%) (disodium salt of ethylene diamine tetraacetic acid)	7.5	60 minutes
	T2 Ion exchange resin [8] (Varion KS)	6.5	14 days
	T3 Trisodium citrate (5%)	7.0	60 minutes
Iron	T1 Hydrogen fluoride (20%)	0.4	10 minutes
	T2 Oxalic acid (5%)	0.4	20 minutes
	T3 EDTA (5%)	6.5	60 minutes
	T4 Ion exchange resin	6.5	14 days
Acid perspiration	T1 Acetone + 5% ammonium hydroxide	9.5	60 minutes
	T2 Non-ionic detergent (0.5% solution of Prävocell)	7.0	60 minutes
Alkaline perspiration	T1 Acetone + 5% acetic acid	6.0	60 minutes
	T2 Anionic detergent (2% solution of fatty alcohol sulphate)	8.0	60 minutes

#### Measuring colour/whiteness before and after treatment

The artificially produced stains were coloured due to their chemical composition and aging. The aesthetic effect of the stain removal method could be measured by colour change of the sample and its whiteness. Colour/whiteness was mea-



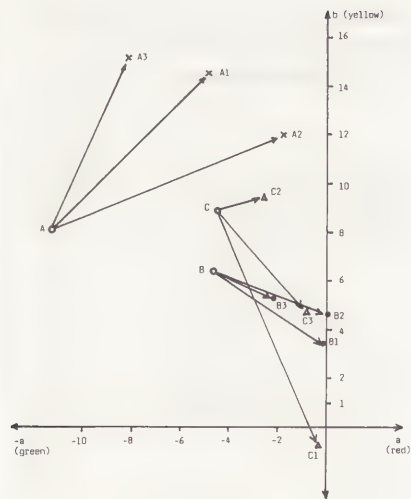


Fig.5. Tristimulus colour coordinates (X,Y,Z) of copper stain before and after removal

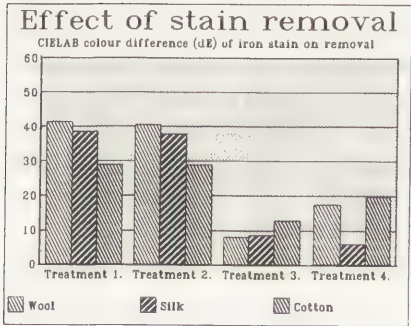


Fig.6. CIELAB colour difference (ΔE) of iron stain on removal

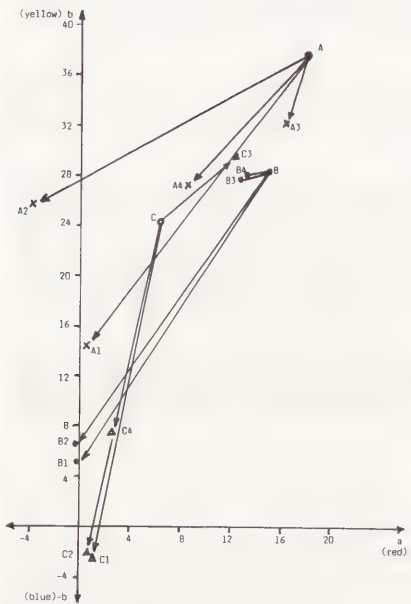


Fig.7. Tristimulus colour coordinates (X,Y,Z) of iron stain before and after removal

sured with a COLOR EYE 3000 reflection spectrophotometer; the measuring geometry was D65/10°, and the diameter of the measured area was 25 mm. The measured X, Y, Z tristimulus colour values were evaluated in CIELAB colour system as well as the colour differences (ΔE\*) (See fig. 1).

Whiteness of the samples were evaluated by BERGER (WB) whiteness (See fig 2.). The Berger formula is defined for an observing field of angular substance 2° and a CIE Standard illuminant C or D65:

$$W_{BE-D} = Y + 3.402Z - 3.897X$$

With the help of the formula, the whiteness of fabrics can be characterised (9).

Measuring tensile strength

Ten yarns of each samples were measured for tensile strength with an INSTRON TM-SM Model. The results were determined by comparing the loss in tensile strength of stained, aged, and untreated samples.

Results for starch on wool, silk and cotton

The colour of the aged stains was yellow. No significant difference of colour (only about 2 ΔE) and whiteness could be experienced on removal. Decrease of whiteness on Treatment 1 was experienced on cotton, most probably due to change of hue from bluish white to yellowish white.

The effectiveness of stain removal of starch was tested using potassium iodate solution. Starch was still present after 60 minute treatments.

Treatment 1 (N-methyl-2-pyrrolidon) caused less loss in tensile strength on all three fabrics. This can be explained by the fact that most probably more starch has been removed by Treatment 2 (diastase enzyme).

Table 2. Loss in tensile strength on removal of starch stain.

Textile	Treatment	Loss in tensile strength (%)
Wool	Treatment 1	0.8
	Treatment 2	6.1
Silk	Treatment 1	4.1
	Treatment 2	8.2
Cotton	Treatment 1	0.3
	Treatment 2	4.0

Table 3. Loss in tensile strength on removal of copper stains.

Textile	Treatment	Loss in tensile strength (%)
Wool	Treatment 1	9.6
	Treatment 2	11.6
	Treatment 3	13.9
Silk	Treatment 1	3.5
	Treatment 2	4.7
	Treatment 3	9.1
Cotton	Treatment 1	0.7
	Treatment 2	9.6
	Treatment 3	15.6

Results for copper corrosion stains on wool, silk and cotton

The colour of the aged stains was yellowish green, which turned to white or yellow on stain removal. Colour differences were between 3–22 ΔE\*. Treatment 1 caused considerable increase of whiteness to cotton.

Treatment 1 (5% EDTA) seemed to be the most gentle on all three fibers, yet effective. Treatment 2 (ion-exchange resin) caused considerable loss in tensile strength, most probably due to the long time (14 days) spent by the fabric in aqueous conditions. The length of the treatment possibly could be decreased. Treatment 3 (5% trisodium citrate) caused the highest loss in tensile strength.

Table 4. Loss in tensile strength on removal of iron stains.

Textile	Treatment	Loss in tensile strength (%)
Wool	Treatment 1	14.7
	Treatment 2	10.4
	Treatment 3	7.2
	Treatment 4	18.4
Silk	Treatment 1	20.2
	Treatment 2	18.4
	Treatment 3	5.4
	Treatment 4	23.0
Cotton	Treatment 1	20.7
	Treatment 2	17.8
	Treatment 3	7.7
	Treatment 4	13.7

Table 5. Loss in tensile strength on removal of acid perspiration stains.

Textile	Treatment	Loss in tensile strength (%)
Wool	Treatment 1	2.3
	Treatment 2	14.4
Silk	Treatment 1	6.8
	Treatment 2	10.3
Cotton	Treatment 1	0.0
	Treatment 2	24.1

Table 6. Loss in tensile strength on removal of alkaline perspiration stains.

Textile	Treatment	Loss in tensile strength (%)
Wool	Treatment 1	28.6
	Treatment 2	17.0
Silk	Treatment 1	23.3
	Treatment 2	13.7
Cotton	Treatment 1	16.0
	Treatment 2	17.6

### Results for iron corrosion stains on wool, silk and cotton

The colour of the aged stains was yellowish "rust-brown." On removal the colour turned to the direction of yellow, hence evaluation of whiteness was useless. Instead of whiteness the lightness was evaluated. Figure 7 shows the colour changes of the samples with CIELAB tri-stimulus colour coordinates. The greatest colour change was caused by Treatment 1 and 2. The effectiveness of the stain removal agents 1 and 2 can be seen on the CIELAB colour difference which is between about 30–40  $\Delta E^*$  (Fig. 6). Increase of lightness was 10–31 on Treatment 1 and 2, while it was 5–10 on Treatment 3 and 4. Improvement of colour and lightness on Treatment 4 was also acceptable.

Treatment 1 (20% hydrogen fluoride) as well as Treatment 2 (5% oxalic acid) caused considerable loss in tensile strength on all three fibers. In comparison to silk and cotton, wool suffered less damage, most probably due to the presence of disulphide linkages in wool which are resistant to acids. Treatment 3 (5% EDTA) seemed to be a rather gentle stain removal method, yet acceptable in effectiveness. Treatment 4 (ion-exchange resin) may have caused the severe loss in tensile strength by the long time the fabric was soaked in water.

### Results for acid and alkaline perspiration stains on wool, silk and cotton

No colour and whiteness change of the stains were experienced and measured on any of the treatments. The presence of residual perspiration agents was not tested.

Treatment 1 (acetone + 5% ammonium hydroxide) did not cause any harm to cotton, but also protein fibers did not lose too much of their original tensile strength. Treatment 2 (non-ionic detergent) must have removed a considerable amount of staining material which caused severe loss in tensile strength of all fibers.

Both Treatments 1 and 2 (acetone + 5% acetic acid, anionic detergent) for removing stains of alkaline perspiration caused considerable loss in tensile strength of all three fibers.

### Conclusions

Investigations of colour difference/whiteness and tensile strength have been proved to be suitable methods for determining the effectiveness and degradation potential of stain removal agents. The samples and treatments in this work were typical and representative of historical textiles. Considering the enormous number of possible stains on historical textiles, similar and more extended research on other stains requires further work. Also, the level of aging, pH, and length



of treatment should be determined for various treatments. Investigation of the stain materials that remain after treatment should be carried out with chemical tests or by other analytical methods.

The conservator's goal to preserve the fabric often does not permit the application of most effective stain removal methods. The compromise between effectiveness and preservation must be made individually with each object.

### Acknowledgements

The authors are indebted to Ágnes Stahl, scientist at the Research Institute for Paints, for carrying out the aging and to Schenker Beatrix, head of the department at INNO-VATEXT Textile Research Institute, and her co-workers for measuring the tensile strength.

### Materials

Cation exchanger "Varion KS" resin ( $-\text{SO}_3\text{H}$  active groups on a styrol-divinyl benzene matrix, granule size 0.3–1.25 mm). NITROKÉMIA INDUSTRIES 8184 Fűzfőgyártelep, Pf. 45. Hungary.

Präwocell non-ionic detergent (ethylene oxide condensates with alkylphenols). BUNA, Germany.

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# Working Group 10

Stone

Matériaux pierreux





## Abstract

The marble slabs covering the walls of the S. Maria dei Miracoli church in Venice are suffering serious degradation due to the combined physical and chemical action of soluble salts. The church walls have a high moisture content due to rain penetration. Laboratory tests and field measurements of the moisture content in various areas of the walls are currently in progress to investigate the thermal and hygro-metric characteristics of the marble slabs covering. The data concerning the indoor climate and its influence on the phenomena are also considered. Knowing the boundary conditions (indoor climate) and using the preliminary data available for the constituting materials (marble), a tentative analysis of the moisture migration in the marble slabs is performed using a numerical model of the heat and mass transfer in porous media. It is shown that the moisture migration, and hence the damages, could be reduced by having a ventilated space between the slabs.

## Keywords

Moisture-induced damage, salt attack, marble, historical buildings, heat and mass transfer, porous building materials

## Influence of Interior Microclimate and Moisture Migration on the Marble Decay in the S. Maria dei Miracoli Church in Venice

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## Introduction

The church of S. Maria dei Miracoli was erected in 16th century by Pietro Lombardo. The brick masonry of the building is completely covered inside and outside with various kinds of marble. People charged with the preservation of the church dedicated great care to the conservation of marble facings. In the 19th century two important restoration projects were carried out and several kinds of marble have been substituted. During the second intervention the new marbles were fixed with Portland cement.

In an attempt to eliminate the capillary rise responsible for the massive presence of salt efflorescences, which in turn in causing the rapid decay of marble slabs, a damp proof course (dpc) was laid in place at the end of 60s. Notwithstanding this intervention the marble slabs continued to deteriorate. Recent studies carried out ten years ago pointed out that the efficacy of the damp proof course was very doubtful because high moisture values were measured below and above this barrier (1).

According to these studies salt efflorescences on marble surfaces were caused by water migration from brick masonry. Only recently during our studies on the origin of moisture in brickwork, the following observations were made. First, there is a high moisture content between 17% and 19% in the range between 1.3 and 3.3 m, which decreases slightly to 13% at 5 m and to 11% at 6 m. Second, the high moisture content measured at high level seems to indicate that water infiltration from the upper part is taking place and this phenomenon is superimposed to the rising damp which was active in the past before they made the barrier. Finally, the old rising damp which was never eliminated since the moisture evaporation from brick was prevented because people did not remove the slabs (2).

The results obtained allow us to conclude that the damp proof course erected at the foot of brickwork has actually prevented further saltwater from reaching the upper brickwork and stopped the concentration increase of the soluble salts. However, the damp proof course but did not remove them, and the salts have continued their aggressive action on the marble surface (1-3). In recent studies, the origin of salt efflorescences seems to be well understood. According to our previous studies the moisture migration causes the transport of salts from the cement mortar. The final result is the formation of massive efflorescences on the marble surface. Salt efflorescences were qualitatively identified by X-ray diffraction and quantitatively by ionic chromatography. Samples 17, 18, and 19 were taken from the surface of the slabs on the side overlooking the canal. Sample 20 was taken from a marble decoration above the entrance door of the crypt. Sample 21 from the wall masonry near the altar. The results obtained are reported in Table 1 (for X-ray diffraction) and Table 2 (for ionic chromatography).

In order to remove or mitigate the primary causes of decay, a highly experimental conservation plan was proposed to desalinate brickwork and stones. It was first

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Table 1. Mineralogical composition of salt efflorescences.

Sample	Thenardite	Aphitalite	Gypsum	Halite	Sylvite	Calcite
17	++++	+				
18	+	++++				
19			++++		+	
20	(+)					++++
21				++++		

Table 2. Quantitative analyses of water soluble anions in salt efflorescences.

Sam- ple	F%	Cl%	NO <sub>3</sub>	SO <sub>4</sub> %
17	0.105	0.033	0.043	74.12
18	0.095	0.133	0.100	56.65
19	0.100	0.027	—	67.73
20	—	0.320	—	0.77
21	0.162	70.640	—	0.34

decided to remove many important architectural and marble parts and to wash them in special containers in order to eliminate the water soluble salts. To evaluate the process of desalination in detail and therefore to find the best methodology to remove salts it was decided to carry out preliminary experiments in laboratory. The laboratory experiments on soluble salts allowed us to affirm that sulfates can be easily removed in one or two days and for this reason we think that they are localized on the marble surfaces. Also, chlorides need more time, probably because they are inside the slab.

As far as the removal process is concerned, it is possible to establish that the sulfate-chloride ratio yields useful information on the kinetic process. By comparing the amount of salt present before and after desalination we can affirm that after two months sulfates are completely removed, while chlorides are only partially removed, about 50% of the total amount initially present.

#### Characterization of the marble slabs

This paper is mainly concerned with the heat and moisture transfer process taking place inside the marble slabs covering the church walls. In this way, the trends of the drying phenomena could be analyzed. An extensive series of tests was performed on the bricks constituting the wall and on the marble finishing, paying special attention to the properties affecting moisture migration. Samples were collected from the walls and used to determine the initial moisture content by weighing them before and after oven drying at 105°C. The pore volume distribution was determined by mercury intrusion. The sorption equilibrium curves were obtained by keeping samples in containers where the relative humidity was kept constant with aqueous salt solutions; these containers were placed in a temperature-controlled cabinet. Continuous monitoring during the year 1990 gave outdoor and indoor temperatures and relative humidities (4). The data concerning the brick walls are reported elsewhere (5).

While many different varieties of marble have been employed in the wall coverings, they all show the same moisture migration behavior. Mercury porosimetry demonstrated that the various types of marble have a very low total porosity  $\varphi$  (ratio of pore volume to total volume), ranging from 0.63% to 1.44% with a pore distribution peak around 1  $\mu\text{m}$  (See fig. 1). Because of this low

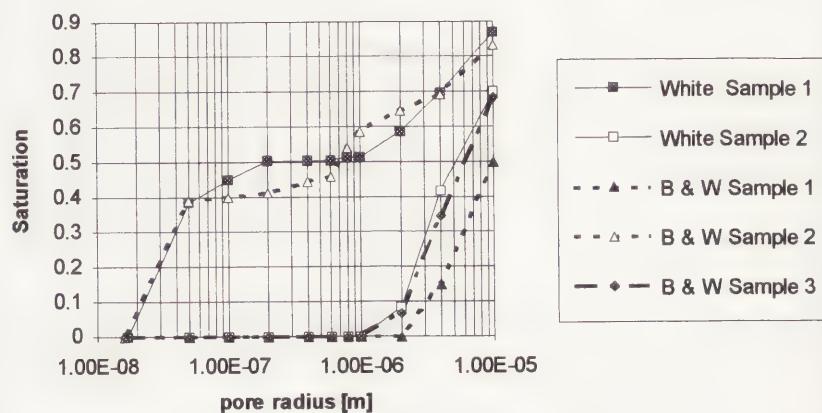


Fig. 1 marble pore size distribution



porosity, close to the sensitivity limits of the method, a great accuracy cannot be expected for these measurements.

The original mass moisture content was very low (about 0.10%). Also, the water vapor sorption was weak: the observed weight increase of the sample sealed in a container was barely noticeable (less than 0.04%); the relative humidity was kept constant at 75.5% with an aqueous solution of sodium chloride (NaCl). From the above data it follows that marble has a negligible capacity to retain water and a very low water permeability and vapor diffusion. For the following calculations, a total porosity  $\varphi$  equal to 1% and an intrinsic permeability  $K$  equal to  $2.0 \times 10^{-17}$  have been assumed.

### **Analysis of the evolution of the marble hygrometric state**

As reported in the introduction, the salt attack is related to moisture migration phenomena. It has been shown that some years are required to obtain a significant lowering of the moisture content of the walls; so, to obtain a satisfactory drying rate, the marble slabs should be temporarily removed or, at least laid in place leaving a void cavity behind them (5). In this paper, we present a qualitative simulation of the drying process assuming that the marble slabs are laid in place leaving a cavity behind them that could be closed or ventilated. Since this research is still at a preliminary stage, the analysis was done using a mono-dimensional model and stationary boundary conditions. Two limit cases were simulated using the average temperatures and relative humidities collected in February and June 1990 for the indoor surface boundary conditions. For the thermal and hygric characteristics of the marble slabs, the rough data available at this time have been used.

### **Global heat and mass transfer model**

Heat and mass transfer in porous media have been object of many studies over the last 50 years. It is now assumed that moisture transfer cannot be interpreted with a purely diffusive model but that the process is strongly affected by capillary suction, temperature gradients, and latent heat transfer due to evaporation and subsequent condensation in the capillary pores (6, 7). A global model of heat and mass transfer is, therefore, required to analyze the moisture migration inside marble slabs, such as that suggested by Whitaker, derived from the researches about unsaturated soils, (8–10). Such an approach has been recently used by other authors (10–12, 14).

Following Whitaker and using the multiphase Darcy equation, three conservation equations are obtained: dry air conservation, water species conservation and energy balance (8). These equations are supplemented with the thermodynamic relations and the constitutive equations needed for the closure of the model. For the details reported in other works of the authors, see Baggio et al. and Baggio and Bonacina (14, 15). This model employs the same equations to represent both the unsaturated and the saturated zone (if present). Phase change phenomena are taken in account as well.

The conservation equations and the other relations needed for the closure of the model have been discretized using the finite element method (FEM), Zienkiewicz, obtaining a non-linear, non-symmetric and coupled system of equations (16). In the same way, the boundary conditions to be imposed at the interface between the tested sample and the surrounding air were discretized, taking in account both the vapor flux and the convective and/or radiative heat exchange. A computer code was written to solve iteratively the non-linear system of equations using the Newton-Raphson method. Time integration was accomplished with a fully implicit scheme. The details of the discretization can be found in Baggio and Bonacina (15). This code was used for the simulation of the heat and mass transfer process in the marble slabs.

### **Results of the simulation**

The 2.5-cm thick marble slab was represented with a mono-dimensional mesh of 40 elements. The transient simulation showed that in all the considered cases,

a steady state condition was reached in less than three years. A variable time step was used that ranged from 1 second for the initial steps to 20 days for the last steps. On both sides of the slabs convective boundary conditions have been imposed, assuming a surface heat convection coefficient  $\alpha$  equal to  $8 \text{ W m}^{-2} \text{ K}^{-1}$  and a surface mass transfer coefficient  $\beta$  (for the water vapor) equal to  $0.072 \text{ m s}^{-1}$ .

For the indoor condition, the average data of February 1990 ( $13^\circ\text{C}$ , 80% RH indoors) were used for the winter period and the average data of June 1990 ( $26^\circ\text{C}$ , 75% RH indoors) for the summer period. The probable evolution of the drying process, considering the variation of the boundary conditions throughout the year, should be halfway between the two limit conditions considered. For both periods, two cases—closed cavity and ventilated cavity behind the slab—were considered. The closed cavity was assumed to be filled with air at 99% RH,  $12.5^\circ\text{C}$  winter temperature and  $25.5^\circ\text{C}$  summer temperature. The relative humidity of the air in the ventilated cavity was supposed to be equal to 85% with the same temperatures as in the closed cavity.

The mass moisture content profiles for the closed cavity are shown in Figure 2 (winter period) and in Figure 3 (summer period). In Figure 4 (winter period)

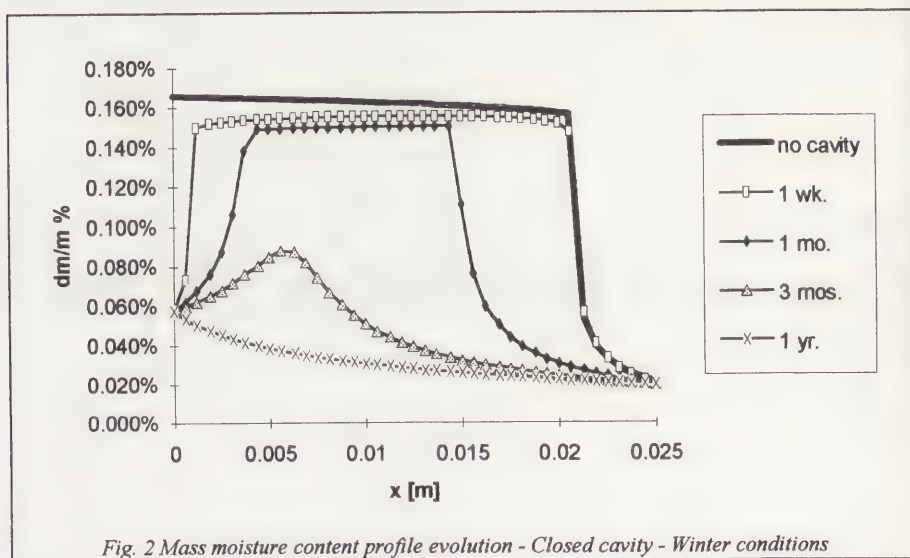


Fig. 2 Mass moisture content profile evolution - Closed cavity - Winter conditions

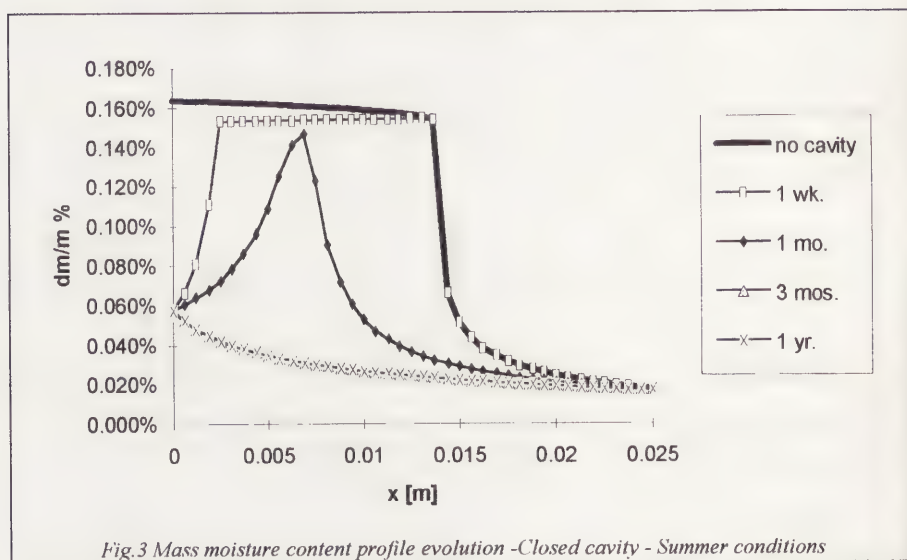
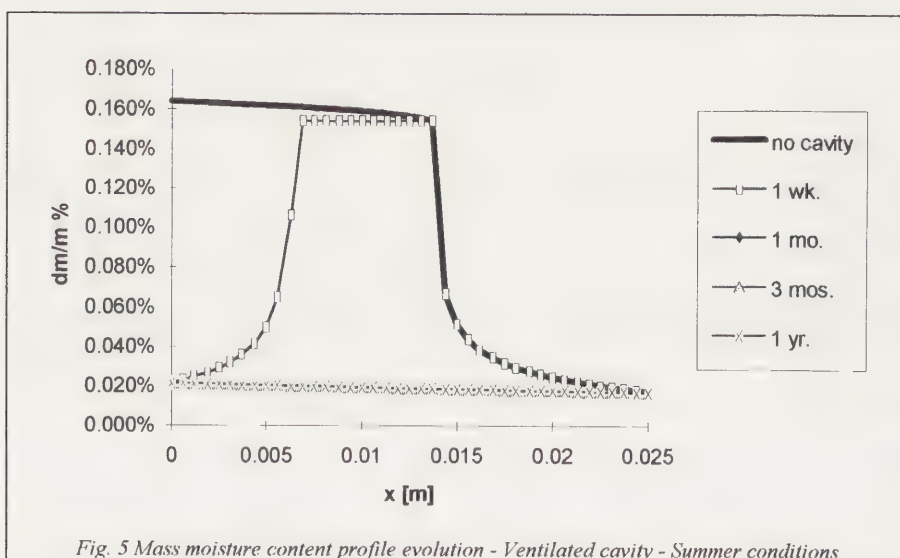
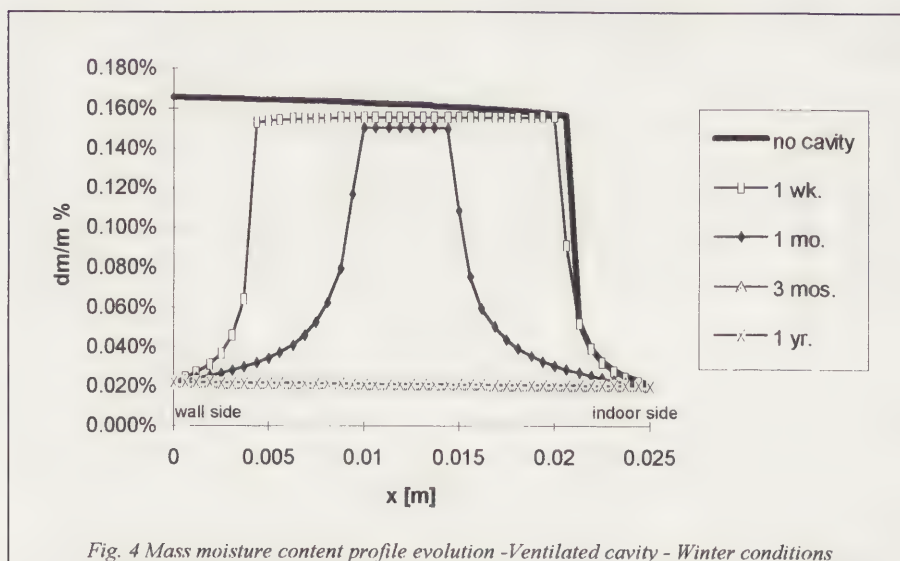


Fig. 3 Mass moisture content profile evolution - Closed cavity - Summer conditions

and Figure 5 (summer period), the profile for the ventilated cavity is presented. All the results are plotted against the moisture profile of the slab when placed in direct contact with the brick wall (continuous thick line labeled "no cavity"), calculated using the same model and considering stationary conditions (i.e., 10% constant mass moisture content inside the wall) (2, 5). The figures show clearly





the effectiveness of the cavity and the strong influence of the relative humidity on the time duration of the drying process.

### Conclusions

This research is still at a preliminary stage, and more work is currently in progress both to classify the moisture transfer properties of the marble slabs and to validate the numerical model with experimental tests. Some qualitative conclusions can, however, already be drawn. The salt removal treatment applied to the marble slabs does not totally eliminate the salts. Therefore, it is of paramount importance to reduce moisture migration phenomena to a minimum to delay the formation of new efflorescences. On the other hand, it has been shown that, even if the marble slabs are removed, some years are presumably needed to significantly reduce the moisture content of the brick walls once the rainwater infiltration has been completely eliminated (5). The numerical simulation presented here suggests that the moisture content of the marble slabs can be kept at significantly lower levels if these slabs are laid in place leaving a cavity, possibly ventilated, behind them instead of placing them at direct contact with the brick wall. These indications should be applied to the restoration work currently in progress.

### Acknowledgements

The authors are indebted to Dr. Giovanna Alessandrini, Director of the G. Bozza CNR Center, Milan (Italy) for the mercury intrusion data, and to Save Venice Inc., New York (USA) for the financial support of this research.

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### Abstract

Marble and stone decay processes were extensively studied on several Venetian monuments in the recent past. According to their texture and structure, stone and marble exhibit a different mechanism of decay. A simplified model of stone decay corresponding to different morphology of deterioration was obtained by examining samples taken by considering the degree of blackness and the degree of sheltering from rain water. Three types of decay were defined: white washing, dirt accumulation, and dirt washing. Two distinct types of spherical particles were found in black dendrite-form crusts: carbonaceous particles with a very porous surface, and smooth particles mainly composed of silicon and aluminum. Airborne particles from combustion of fuel are very efficient catalysts of the sulphuric acid formation from sulphur dioxide oxidation.

### Keywords

Marble decay, carbonaceous particles, Istrian stone, Carrara marble

## The Weathering Mechanisms of Marble and Stone Venetian Monuments in Relation to the Environment

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### Introduction

Historical photographic documentation carried out at the beginning of this century shows that most of the Venetian monuments were covered by soot deposits. However, they did not present heavy deterioration processes. This means that the stone and marble of Venetian monuments deteriorated very slowly when they were exposed for centuries to natural weathering agents. The stonework made some centuries ago has started to deteriorate very quickly in recent decades when industrialization and urbanization reached the Venetian province.

In a previous paper we correlate the marble decay of Venetian monuments to certain atmospheric pollutants (1). A careful observation of the damage taking place on the surfaces of building materials shows that large amounts of substances were absent (or present in small amounts) in the original material. In most Venetian monuments studied, the stone decay was ascribed to the transformation of calcium carbonate into calcium sulphate. This phenomenon is commonly observed elsewhere and has been discussed by many authors.

Previous work carried out by the present authors and other researchers has demonstrated that gypsum formation is caused by sulphuric acid; this acid is, in turn, formed by sulphur dioxide oxidation (2-5). As a consequence, the presence of sulphur dioxide is a necessary condition for the gypsum formation, but it is not the sole condition; other factors are involved. Starting from this consideration we have attempted to improve the knowledge on the mechanism of stone decay.

The oxidation of  $\text{SO}_2$  into  $\text{H}_2\text{SO}_4$  in the atmosphere has been studied extensively (6-8). The most recent work in this area was published by Beilke, who established that sulphur dioxide is oxidized in the atmosphere by the following mechanisms: homogeneous gas phase reactions in aqueous droplets and on surfaces of aerosols, and heterogeneous  $\text{SO}_2$  oxidation in cloud droplets or on aerosol particles (9). From this work, it is evident that more emphasis is now reserved to the action of ozone and hydrogen peroxide in the troposphere, with respect to the catalytic oxidation by trace metals, than was previously considered important. Minor importance is reserved to the oxidation of  $\text{SO}_2$  onto the carbonaceous particles.

Some researchers have recently pointed out that carbonaceous particles are the only responsible mechanisms for decay processes. But they did not report experimental evidence to support their hypothesis. In our opinion, we must first consider the presence of high  $\text{SO}_2$  concentrations and the possibility that part of the  $\text{SO}_2$  is transformed in the atmosphere according to the different mechanisms proposed in the literature (6, 9, 10-12). The remaining part of  $\text{SO}_2$  that reaches the stone surface can be oxidized in the black crusts by catalysts of atmospheric origin (such as trace metals or carbonaceous particles). The last, but not least, consideration is the influence of moisture coming from rainwater or condensation processes.

Air pollution measurements carried out in Venice since 1972 have demonstrated that winter periods are the most dangerous. At this time, the different factors influencing the sulphur dioxide oxidation are contemporaneously present. The action of acid sulphur gases on calcareous materials is strongly dependent on the morphology of the surface and on the intrinsic properties of the stone such as mineralogy, texture, and structure.

As far as the morphology of the surface is concerned, black and white areas are generally correlated to different degrees of decay due to the different mechanism



of deterioration involved. We can also observe a different degree of deterioration with regard to the black scabs. In an effort to build a model of stone deterioration, this point will be demonstrated in this paper through experimental evidence. With regard to the intrinsic properties of the stone, we also compare the different mechanisms of decay taking place on various limestones, characterized by different textures and structures. The modelling of stone deterioration is difficult to develop; each monument must be studied in detail, as each monument presents different behaviours due to the various factors involved.

### Analyses of deteriorated marble and stone

To assess the different process of decay, surface samples of decayed stone were taken from different monuments according to the following criteria: the degree of decay through macroscopic observation, the orientation of the individual architectural elements, the exposure to direct rainfall (washed areas), and the degree of shelter from rainwater (black areas).

To identify the chemical and mineralogical composition of decayed stone, X-ray diffraction and high performance liquid ion chromatography were carried out. The morphology of the decayed layer was studied using scanning electron microscopy (SEM) to examine the shape of the crystals, and energy dispersive X-ray analyses (EDAX) was performed to detect the amount of the elements present. Optical microscopy of cross sections was also done to observe the different layers formed on the surface.

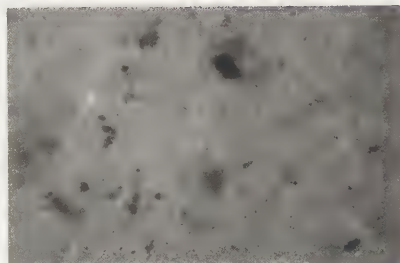


Figure 1. Microphotograph of carbonaceous and iron oxides particles.



Figure 2. Spherical metallic particle mainly composed of Si and Al.

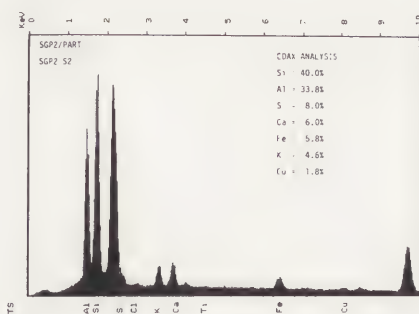


Figure 3. EDAX spectrum of the Si/Al spherical particle.

### Airborne particles in the atmosphere and in the black crusts

Pollutant particles present in the Venetian area were examined microscopically on filter papers. Carbonaceous particles having a spherical and globular shape, a sparkling appearance, and a variable diameter (7–40 microns) were the most prevalent. Other particles with an earthy yellow or brown appearance were identified by microanalytical tests as iron compounds; these particles were much less abundant than the carbonaceous particles (fig. 1). The smallest particles of the black carbonaceous material often formed aggregates, while the larger, uniform, opaque ones (some with diameters > 1mm) are less numerous. Rarer yet are the small spheres not identified at the optical microscope; these particles were metallic in appearance, bronze coloured, highly reflective, and were 30–80 microns in diameter. By means of chemical attack, some of the particles were isolated and examined by using a SEM-EDAX. The EDAX spectrum shows an aluminosilicate composition, as well as clearly prevalent quantities of silicon and aluminum.

The most abundant component of black crusts visible in the optical microscope are carbonaceous particles; these are mainly spherical with a glass-like transparent or opaque appearance. Their dimensions correspond well with the ones already observed in the filters. Carbonaceous particles are sometimes rounded and sometimes link together to form large, irregular aggregates.

For more precise identification, the same samples were analyzed by a SEM interfaced with an X-ray dispersive energy analyzer (EDAX). At high magnifications, spherical particles of different sizes and appearances can be distinguished. The particles are typical (in shape and size (SEM), colour (optical microscope), and chemical composition (EDAX) of incomplete combustion of coal- or oil-fired power plants.

Two different types of spherical particles can be distinguished: the smooth ones and the porous ones.

During combustion, minerals containing aluminosilicate and iron compounds melt and form liquid drops, which during emission in the chimney are rapidly cooled and form glass spheres. Those with a smooth surface have a metallic composition; the prevailing components are silicon and aluminium with minor components of iron always present, in addition to other metals such as titanium or copper (See figs. 2, 3). Among the non-metallic components are significant amounts of calcium and sulphur. The composition of these smooth particles is typical of aluminosilicate compounds which come from clayey impurities in



original fuels. Sometimes smooth, spherical particles entirely formed of iron can be found. Pure iron particles are less frequent than the silicon/aluminum spheres. Non-metallic contributions of calcium and sulphur are always present, and indicate the potential of these particles for the formation of gypsum crystals on their surfaces. This process is clearly visible on the stone surface, but it does not appear to be very important as a nucleating process as was emphasized by some authors (13).

The second type of particles, the porous ones, are characterized by a rough surface completely different from the smooth particles previously described. The surface cavities have different sizes and depths, and the specific surface of the particles is very high when compared to a smooth spherical particle of the same radius (See fig. 4). This property is very important. From an industrial point of view, it is very well known that the use of carbonaceous particles favours oxidation processes. A logical consequence of this behaviour is to ascribe to carbonaceous particles a fundamental role in the formation of sulphuric acid, which in turn causes the gypsum formation (fig. 5).

### Morphology of decay and interpretation of the related deterioration mechanisms

In a previous work, we observed that the areas sheltered from direct rainfall and from surface runs are generally covered by a thick and hard black crust with a rough and spongy appearance which is sometimes in dendrite form (14). The black surfaces collect atmospheric particles and represent a growth zone in which the transformation of calcium carbonate into gypsum takes place.

Some characteristics marking patterns frequently observed on buildings surfaces allow us to distinguish three types of decay: dirt accumulation, dirt washing, and white washing (15). Dirt accumulation and dirt washing are confined to black areas sheltered from direct rainfall and from surface runs.

Dirt accumulation takes place far from rain washing areas and is characterized by black superficial deposits that grow on the surface due to the collection of atmospheric particles and to the transformation of calcium carbonate into gypsum.

Dirt washing takes place at the interface between running water and sheltered areas. The thick and hard black crust that forms has a rough and spongy appearance, and grows with respect to the original surface (See fig. 6).

In white washing areas, which is the third type of deterioration observed, the formation of a surface skin is prevented because the stone is exposed to the washing action of the rain; this has the effect of removing both the soluble compounds which would otherwise form a skin and the deposited soot. As a consequence, skin formation does not occur in rain-washed areas.

This simplified model of the complex mechanism of marble and stone decay was tested on several Venetian monuments. The results obtained have pointed out that the features visible on stone surfaces correspond to different degrees of deterioration. Careful observation suggests that sulphates are present in different amounts according to the degree of sheltering irrespective of differences in stone texture-structure.

The degree of sulphatation in protected areas was found to depend on the distance from the rain washing areas. In areas far from running water where dirt accumulation takes place, the degree of sulphatation is generally less than 40%. In areas located at the interface between washed and unwashed areas where dirt washing takes place, the degree of sulphatation is larger than 40% (See table I).

### Analyses of deteriorated layers of Istrian stone

We consider now the different mechanisms of decay taking place on marble and limestone that are characterized by different textures and structures; both Istrian stone and saccharoidal marble will be discussed.

Istrian stone is a very compact, microcrystalline limestone (with a colour variable from grey-green to pale yellow) with a few sedimentation and stylolitic dis-

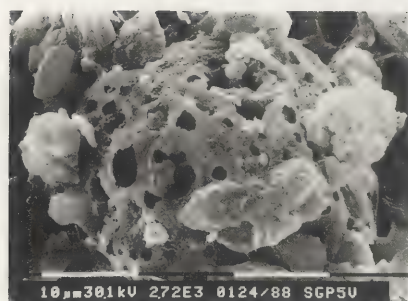


Figure 4. Carbonaceous spherical particle.

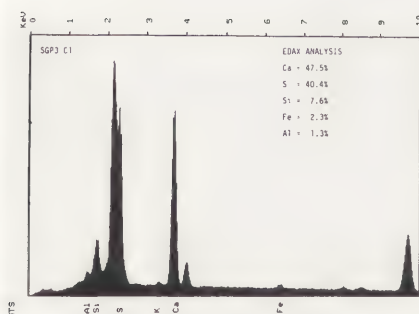


Figure 5. EDAX spectrum of carbonaceous particle.

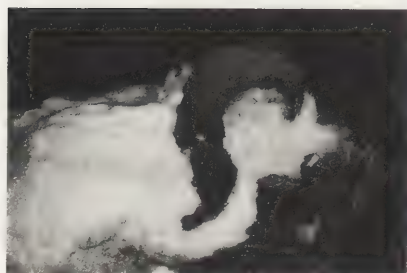


Figure 6. Black crust with a rough and spongy appearance.

Table I. Percentages of soluble sulphates from samples taken from the third arch, representing the Arts and Crafts, from main Portal of Saint Mark's Basilica.

Arts and Crafts	Black crust near dirt washing		Black superficial deposit	
Butchers (4th panel from the left)	SM 1	67.3%	SM 2	40.3%
	SM 3	56.4%		
	SM 15	64.3%		
Butchers (5th panel from the left)	SM 4	56.8%	SM 5	29.6%
			SM 16	32.5%
Fishermen (1st panel from the right)			SM 21	32.6%
			SM 22	41.5%

solution planes. The presence of micropores (characterized by homogeneous and compact areas) and macropores (formed by heterogeneous areas) is responsible for two opposite phenomena: durability and extensive exfoliation and scaling. The good durability of this stone is evidenced by its ability to withstand centuries of exposure to the aggressive marine and urban environment of Venice. On the other hand, the presence of extensive exfoliation and scaling occurs in poor quality stones containing abundant clay impurities along the sedimentation beds.

Dendrite-shaped black crusts, black superficial deposits and white superficial deposits were analyzed on different monuments. The soluble anions present were mainly sulphates followed by small amounts of chlorides, nitrates and fluorides.

With regard to the amount of sulphate present, it is evident that this depends on the type of black incrustation. For instance, the thick black dendrite-shaped crusts (growing from the surface toward the outside) contain high amounts of sulphates: from 20 to 28% in Ca' Pesaro, and from 40 to 46% in the Doge's Palace.

If the surface is very compact, gypsum formation can take place on the surface without penetrating; on the contrary, when the surface presents microcracks or sedimentation beds, a penetration of sulphuric acid solution can occur; this causes the formation of a white powder of gypsum in the interstices between scales provoking the exfoliation of the stone.

Other black areas characterized only by a superficial deposit show a minor amount of sulphates. In this case the gypsum formation affects the stone only in the superficial layer without penetrating in depth.

Running water causes the formation of a white thin layer tightly adherent to the stone. The analytical data show the presence of low amounts of gypsum and large amounts of recrystallized calcite. In white superficial deposits the amount of sulphates is below 1%. In this case, the high solubility of calcium sulphate does not allow the formation of a thick gypsum layer.

As regards the other anions we can observe that chlorides are generally present in amount, below 1%; only in five cases we measured higher amounts. Chlorides, contrary to sulphates, being strictly correlated with air pollutants, are dependent on the deposition of marine aerosols. In the lower parts of buildings, the presence of chlorides can be ascribed to salt migration from the water of the lagoon by means of rising moisture.

#### Analyses of deteriorated layers of saccharoidal marbles

Saccharoidal marbles are very pure metamorphic limestones, characterized by a crystalloblastic structure and calcite crystals with a density between 0.85 and 1.25 cm<sup>3</sup>/100 g.

According to Kessler, thermal changes can cause a permanent expansion on marble, very probably due to a slipping of the individual calcite crystals against



one another (16). According to Marchesini, the weathering of marble is at first purely physical due the increase in the porosity caused by thermal changes (17). For instance, in experiments carried out on different types of saccharoidal marbles, the porosity increased by up to 40–50% of the original material when they were subjected to fluctuations of temperature of 50°C. The increase of porosity is caused by the marked anisotropy of calcite crystals (when an increase of temperature takes place, the crystal expands in one direction and contracts in the traverse direction). Such movements cause an internal cleavage of crystals and detachment of one crystal from another.

Saccharoidal marbles which have suffered an increase in porosity are easily attacked by other agents, in fact, the circulation of water containing soluble salts is favoured by the increase in porosity. A careful examination of Carrara marble from the Basilica of St. Mark and the Portal of SS. Giovanni and Paolo church indicate the presence of two different morphologies of deterioration.

For the first morphology, on the surfaces directly exposed to rainwater, the superficial granular disaggregation rate due to natural agents (such as thermal changes) was strongly accelerated by the decreasing pH of acid rain of polluted urban environment.

For the second morphology, on sheltered areas, the transformation of calcium carbonate into gypsum is more active (18). The microcracks generated by thermal changes are easily penetrated by sulphuric acid solutions which attack the edges of calcite crystals forming calcium sulphate. The final result is a disaggregation of calcite crystals and the crumbling of large pieces of marble, exposing the underlying surface to the aggressive action of atmospheric pollutants. The emerging surface is white and lacks cohesion (See fig. 7).

In the "Saint Mark's Basilica," we compared the amount of sulphates found at the beginning of 1970s with those analyzed 15 years later. The increasing amount observed in the present survey does not appear to agree with the measured decreasing trend of sulphur dioxide concentration. This is only an apparent contradiction, as the marble has a memory effect and all the decay products accumulated on the surface remain active when the pollution is decreased.

Samples of black crust have, in most cases, a gypsum matrix clearly recognizable by the typical acicular or platy habit of gypsum crystals (See fig. 8).

Gypsum appears on marble as a result of attack by sulphur dioxide and tends to have the characteristic lamellar flower structure. The primary gypsum forms on calcite crystal surfaces along the intergranular spaces (See fig. 9); it is found at progressively deeper locations below the surface with increasing duration of exposure to the polluted atmosphere. Secondary, i.e. recrystallized, gypsum forms at exposed surfaces, where it is deposited by evaporating absorbing water and often builds a massive crust, the thickness of which is proportional to the period of exposure and the frequency of wet-to-dry cycles.

### Conclusion

Conclusions can be drawn about airborne particles, different degrees of sulphatation, and different lithotypes.

The analyses of dendrite-form black crusts have shown the presence of metallic spherical particles embedded in a close net of gypsum crystals. As far as the spherical particles are concerned, we have observed in the SEM two different morphologically distinguishable types: porous and smooth. The porous ones characterized by an irregular surface are composed of carbonaceous particles. EDAX analyses of carbonaceous particles show a high sulphur content. The smooth ones are mainly composed of silicon and aluminium from, aluminosilicates, and by small amounts of other metals such as iron and titanium and discrete amounts of calcium and sulphur. Sometimes smooth spherical particles were almost entirely composed of iron oxides. According to Cheng et al. (19), particles with a porous surface come from the combustion of oil-fired fuel, while particles with smooth surface seem to be typical of coal combustion. The porous carbonaceous and the smooth spherical particles of aluminium and silicon are very active as catalysts in the transformation of calcium carbonate into gypsum.

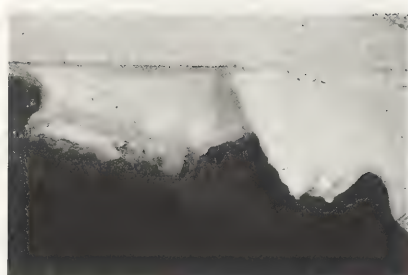


Figure 7. Decohesion of calcite crystals cause crumbling of pieces of marble.



Figure 8. Gypsum crystals.

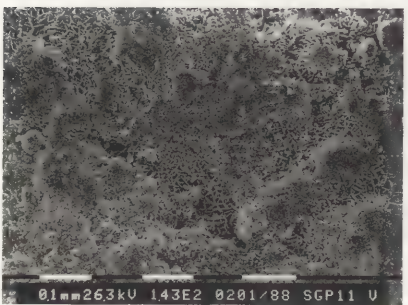


Figure 9. Large crystals in between microcracks and small gypsum crystals on the cracks.



Quantitative data obtained by samples taken by considering the degree of blackness and the degree of sheltering from rain water allow us to make a simplified model which correspond to a different morphology of deterioration. Three types of decay are generally distinguishable on the surface of the monument: white washing, dirt accumulation and dirt washing. Dirt accumulation and dirt washing are confined in black areas and represent two different morphologies of decay which are dependent on the distance from the rain washed areas (6). The dirt-washing area takes place at the interface between running water and the more sheltered areas. The thick and hard black crust has a rough and spongy appearance and grows with respect to the original surface. The dirt accumulation takes place far from rain washing areas in well-sheltered areas and is characterized by black superficial deposits that accumulate on the surface due to the precipitation of atmospheric particles. The results obtained show that the sulphate formation is greater in the black dendrite-shaped crusts which are generally formed in the interface between the white-washing areas and the sheltered ones. In this area the sulphuric acid formation is more efficient because the stone remains moist for a longer time than the inner sheltered area due to the migration of water from the washed areas.

The macroscopic observations show that, despite the fact that various type of stone all comprise calcium carbonate and are exposed to the same environment, they nevertheless exhibit different types of deterioration. The parameters responsible for this different behaviour are the intrinsic properties of the stone (texture and structure) and the geometry of the monument (degree of shelter from rainwater). After the removal of the black scabs, the Istrian stone appears to be in a good state of conservation, indicating that decay is only superficial, probably due to the low porosity of the stone that does not allow the penetration of liquid water and consequently limits any deterioration process. The white marble is severely damaged due to the different texture of calcite grains which, after a certain time, allows water to penetrate into intergranular spaces, and favours the reaction of acid sulphur-bearing solutions which form gypsum around the grains. This is the starting point from which a progressive attack of calcite marble takes place. Contrary to the case of the Istrian stone, there is a penetration of gypsum crystals inside the marble which causes an intimate mixture of original calcite, gypsum, carbonaceous particles and natural or man-made atmospheric dust. The black scab formation causes heavier decay phenomena with respect to the ones observed on Istrian stone.

### Acknowledgements

The author wishes to thank P. Fuga for typewritten and graphical support, D. Zanella for the SEM analyses and photographs, and M. Rossetti for cross sections and X-ray diffraction.

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## Abstract

Investigations and conservation treatment of the 10th century Lednica Castle - the most important and best preserved remains of a palatine-type Royal Castle in Poland. The materials were hard, resistant boulder stone and weak, porous gypsum mortar. Investigations determined the morphology of mortar decay processes as well as methods for its consolidation with an inorganic, clear solution as a recrystallizing agent. The paper presents an advanced preservation technique and treatment method for monuments undertaken by the Museum of First Piasts at Lednica within the broader context of environmental protection.

## Keywords

Consolidation, stone relics, environment, historic preservation, gypsum mortar, recrystallization, Landscape Park Lednica, open air museums, archaeological, ethnographic



1. Map of Lednica Landscape Park. 1. concave castle, 2. coniform castle, 3. compass of Lednica Landscape Park, 4. interior area of the Park. (Copyright Muzeum Pierwszych Piastów na Lednicy.)



2. Lednica Island, aerial view. (Copyright Muzeum Pierwszych Piastów na Lednicy.)

## The Conservation of Stone Archaeological and Architectural Relics at Lednica Island—Research and Treatment

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## Introduction

The Earth Summit—the United Nations Conference on Environment and Development held in Rio de Janeiro, June 1992—recommended that more action be taken on environmental concerns. Unesco and ICOM are urging that more attention be paid to environmental protection and at its 16th General Conference in Quebec, ICOM approved the recommendation that museums should develop more varied activities in this field. The Polish National Committee of ICOM and its Conservation Commission have participated in many projects where efforts were carried out to promote specific, advanced protection techniques and conservation methods of monuments, museum collections and other cultural heritage.

A case study is presented here that deals appropriately with advanced laboratory investigations on the topic, as well as with actual practical work that must be expanded in some respects, as for example to matters of importance in the broader aspects of protection against the pernicious influence of environmental contamination. The Muzeum Pierwszych Piastów na Lednicy (Museum of First Piasts) is an example of an eco-museum, which administers two archaeological and one ethnographic museum, as well as several ethnographic objects preserved 'in situ' and a broad landscape park around Lednica Lake (See fig. 1). It is believed that this type of museum may fulfil an essential role in contributing to an understanding of the need for complex preservation measures for our cultural heritage and the environment.

## The object

Inside the circle of a huge wooden and earthen rampart on Lednica Island (See fig. 2) lay the best preserved and most representative remains of the early medieval palatine-type Royal Castle, which from the 10th to the 12th century AD belonged to the first Polish kings. The chapel, palatium and separate church were masoned. The rest of the buildings on the island were made of wood. There are no records dealing with the construction of the castle. It has been examined and excavated since the middle of the 19th century by numerous investigators. Because of the size and significance of the ruin to Polish medieval history, the Ministry of Culture, Direction of Monuments Care and Museums selected it in 1950 as the site in which to perform further systematic excavations, structural conservation and restoration and, in so doing, to formulate a model for proper study, restoration and maintenance throughout the Lednica complex. The life of the monument has been marked by periods of use alternating with demolitions in 1038 and later, until 1331 when it was abandoned and neglected (See fig. 3). We know of a first preservation effort about 1870. Others were carried out in 1927–28 with the removal of brushwood overgrowing the ruins. Since then some restoration has been undertaken every year.

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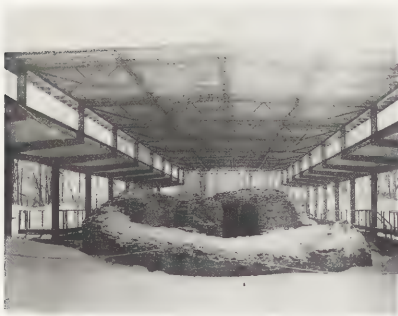




3. The ruin of the Castle, 19th century drawing. (Copyright Muzeum Pierwszych Piastów na Lednicy.)



4. The ruin under a wooden lean-to, from 1950 to 1977. (Copyright Muzeum Pierwszych Piastów na Lednicy.)



5. The ruin under island station roof, after 1978. (Copyright Muzeum Pierwszych Piastów na Lednicy.)

On the outside of the ruin, close to the palatium, the whole west gable end has fallen down. This recumbent part of the castle has remained unscathed since medieval times when it caved in. In 1950 a wooden lean-to was erected above the ruined palatium and chapel (See fig. 4) and in 1978 this was replaced with a new island station roof made of steel and copper, in order to shelter the object from snow and rainfall (See fig. 5). In 1969 the Museum of First Piasts was created and in 1979 it was expanded into a multipartite institution with a landscape park. Since 1982, an interdisciplinary team of scholars and scientists works in the Museum and since 1989, a commission for the conservation of the whole object. The most important task of the commission is the conservation of the ruined castle (1).

Materials and working techniques

Masons' materials have varied remarkably throughout history. For the walls of Lednica Castle, as for other very early medieval architecture in central Poland, broken boulder stone and gypsum, gypsum-lime or lime-clay mortars were mainly used (2). All kinds of boulder stones in walls were identified petrographically by J. Skoczylas (See Table I). Vaults, wall facings and details were made partly of calcareous sinter.

Table I. Petrographic determination of stones in lower parts of walls at Lednica Castle.

Rock	Chapel		Palatium	
	Number of samples	%	Number of samples	%
Gneises	56	50.4	107	60.1
Granite	24	21.6	30	16.9
Quartzsandstone	9	8.1	29	16.3
Quartzsandstone "Jetnice"	15	13.6	7	3.9
Porphyry	—	—	5	2.8
Gabbro	4	3.6	—	—
Amphibolite	2	1.8	—	—
Syenite	1	0.9	—	—

After: J. Skoczylas.

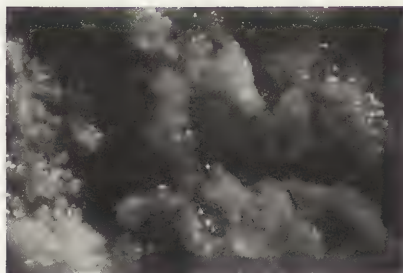
The first analyses of mortar from Lednica Castle were performed about 1870. They showed the presence of gypsum with the addition of lime. Further chemical analyses done in 1953, 1956, 1980 and 1989 confirmed that the main constituent was calcium sulfate and secondarily calcium carbonate with some in acid-insoluble residues. The analytical data are sufficiently numerous and accurate to determine great variability in the composition of mortar used for laying the stone in the walls. (See Table II).

Table II. Chemical analysis of mortar samples from Lednica Castle.

Sample	Place	Content %			Structure	Tinge
		CaSO <sub>4</sub>	CaCO <sub>3</sub>	Insol.		
6	Chapel	96.76	1.96	0.95	dense	y.-r.
8	Chapel	95.32	3.85	0.90	dense	y.-g.
9	Chapel	70.78	13.72	15.30	dense	p.-g.
10	Chapel	81.79	3.02	9.80	dense	p.-g.
11	Crypt	54.56	42.95	2.54	porous	w.-y.
12	Palatium	83.85	6.30	3.80	porous	y.-g.
14	Palatium	94.96	4.13	0.90	dense	w.-y.
16	Palatium	96.04	0.56	2.10	dense	w.-y.
22	Palatium	95.50	1.96	1.20	porous	p.-b.
23	Palatium	0.82	88.70	9.80	powder	y.-b.
25	Palatium	55.10	43.30	1.36	porous	g.
26	Crypt	54.62	43.00	1.45	porous	y.-g.

b = brown, g = grey, p = pink, r = red, w = white, y = yellow.  
After: PKZ—Cracov (Wirska-Parachoniak).

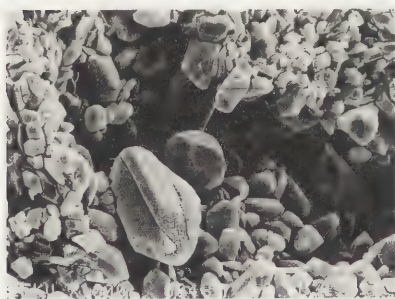




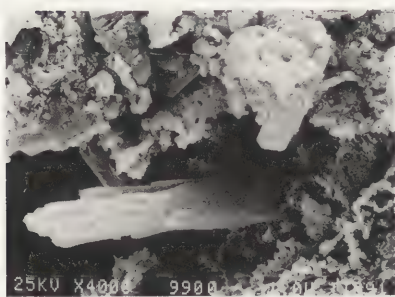
6. Microphotograph, gypsum-lime mortar, reflected light, magnification 25×. (Copyright Muzeum Pierwszych Piastów na Lednicy.)



7. S.E.M.-graph, crystalline structure of gypsum mortar. (Copyright Muzeum Pierwszych Piastów na Lednicy.)



8. S.E.M.-graph, bigger gypsum crystals inside pore. (Copyright Muzeum Pierwszych Piastów na Lednicy.)



9. S.E.M.-graph, gypsum mortar decayed to a great extent. (Copyright Muzeum Pierwszych Piastów na Lednicy.)

Macro and microscopic examinations showed the great heterogeneity in samples of mortar from the inner core of the walls (See fig. 6). The mortar is white gypsum, more or less smooth putty of different coherence, from dense to disintegrating into powder. Small rounded particles of red ceramic, black charcoal, brown iron oxides and oblong plant fibers in small quantities dispersed in some areas are responsible for reddish, yellowish and grayish tinges.

Some samples of mortar were analyzed by scanning electron microscope (SEM). A big advantage over an ordinary optical microscope and wet analysis is the possibility with the SEM method, supported by x-ray diffractometry (XRD), to distinguish gypsum as the binding agent, and anhydride, calcite and quartz in the mortar.

The gypsum and lime in the binding medium have heterogeneous crystalline structures, so that in such cases other samples from the same wall fragment are necessary for comparison and for a more representative analysis. The investigations made by SEM show the clear crystalline structure of the material. The characteristic morphology of gypsum crystals is shown in the SEM micrograph (See fig. 7). The crystals differ very little in size. The micrograph on fig. 8 shows bigger crystals, having maximum dimensions of about 4 mm, growing within the pores of gypsum putty. But other micro-areas show different characteristic crystal growth patterns, which differ from typical gypsum; there are very small, irregular particles (See fig. 9). This type of pattern proves that the material has deteriorated to a high degree (3).

Other lime-sand mortar was used in restorations from 1927 to 1939 to fill in lost original mortar between stones. To set a wall cap of loose original stones, strong lime-cement-sand mortar was recently prepared. Fragments of reddish gypsum plaster on the outer sides of walls, yellowish in window cavities and doorways, and grayish on floors provide information on how the castle looked in the Middle Ages.

### Deterioration

The deterioration of the walls was affected mainly by the presence of water percolating through the masoned walls and the effect of frost (4).

The effect of water is threefold: it can dissolve the binding medium; it can carry dissolved components and it can rupture porous structures when it freezes. Dissolution and disintegration of binding gypsum medium will decrease the mortar cohesion, considerably weakening the structural stability of the walls. As a consequence the vaults and upper parts of the walls fell to ruin and the standing ones are susceptible to crumble into rubble. Obviously, those areas where the mortar is more porous and heterogeneous disintegrate faster than those where it is more uniform and dense (5). Further factors responsible for the damage include the penetration of ground water into the monument's foundations, increased contamination of the soil and water, the increase in air pollutants in the atmosphere (6), biological growth as a result of fertilizing fields and waste water flow producing hypertrophy of the lake.

A permanent increase in air pollutants comes from industrial areas, transported long distances along atmospheric fronts; as well as from local motor vehicles, power stations, factories and stoves which release contaminants into the atmosphere by the combustion of coal and other fossil fuels; and also from the putrefaction of great masses of organic material. The analytical result of the contamination of air, water and soil may be slight, but the cumulative reaction of environmental contamination on the monument can be considerable over a long period of time. In addition, the synergistic effects of nitrous-sulphur combined with pollutants in the presence of humidity is cited as the most influential factor in deterioration.

Organic growth on stone relics in Lednica visible to the naked eye is usually green and grayish-brown and occurs at warmer periods of the year in lower, humid parts of the walls under shadow; it consists of algae, mosses and lichens especially on north-facing surfaces, as well as plant vegetation outside the sheltering island station roof. The plant roots also play a considerable role in the



chemical deterioration of the stone material. Experimental studies show that the chemical action is exerted by the activity of acids produced by the rootlets and by the excretion of inorganic and organic compounds with etching and chelating capabilities.

The role of sulfo-oxidizing bacteria, mostly from the *Thiobacillus* genus, as well as of ammonia and nitrite oxidizers of the genera *Nitrous* and *Nitrobacter* in the different stone materials has been reported many times. The effect of their activity may be considerable and comparable to that of 'acid rain'. Additionally they take the initiative in starting chains of chemical reactions and biological vegetation.

### Conservation

Since 1989 the authors have had the opportunity to develop an integrated program of study and treatment of the ruin of Lednica Castle. A commission composed of scientists, chemists, mineralogists, material technologists, conservators, an historian and an archaeologist works on the project. Our Commission collaborates closely with the Interdisciplinary Team of the Museum comprising scholars, scientists and practitioners. We believe that this specialized cross-disciplinary interchange of thought has allowed for a far more efficient use of knowledge, experience and skill, and for a fuller exchange of information, which enhances the perspective of restorers and researchers alike (7).

In spite of all former conservation efforts, there are still some outstanding problems to be solved at Lednica Castle. These can be summarized as follows:

- \* Whether the island station roof adequately protects the ruin of the castle from water penetration from rain and snowfall.

As to protection against the penetration of rain water, it should be noted that there are prevailing wet and moderate winds from the west and south-west year-round, but they are dry and hot in summer and icy in winter from the east and north-east. This results in the erosion of buildings and monuments mostly on the west and south faces. Therefore the protection against rain and snowfall from the west and south should be improved through better screening, extracting soluble salts and hydrophobing walls. A project for further work has already been prepared and has been recently discussed. It should improve the efficiency of protecting the castle ruin as well as correct its aesthetic appearance, so that does not disfigure the landscape.

- \* Whether the decreased stability of the walls is still strong enough to ensure a durable integrity of the object.

The gypsum and gypsum-lime mortar inside the walls of the castle are weak. In spite of filling lost mortar between the stones with new lime-sand mortar and setting a wall cap on the top with strong lime-cement-sand mortar, some outer parts of the walls are inclined to fall into ruin. The solution to this problem is consolidate the weakened mortar.

In 1989 a series of laboratory experiments was carried out on the consolidation of gypsum and gypsum-lime mortars by means of different organic and inorganic consolidants in order to evaluate the efficiency of various procedures, separately or in conjunction with desalination. Based on the results received, the elaborated method of desalination and consolidation was tested in 1990 on a 2 meter-long section of the southern wall of palatium, so far successfully.

The desalination was carried out prior to consolidation by repeated soaking with water and at the end by poulticing. The argillaceous poultice was separated from the surface with moist, strong Japanese tissue. The consolidating solution was introduced into the wall by repeated pouring into the mortar joints through bored holes. It contained a saturated, clear water solution of active magnesium, calcium, aluminum silicates and barium hydroxide with a small addition of urea and colloidal active silica. The solution must be prepared fresh every time, because little by little it loses its activity after some minutes.

- \* Whether the growth of algae, mosses, lichens and micro-organisms is playing a significant role in the deterioration of the object.

Biological examination performed by K. Lutomski at the Agriculture Academy in Poznan indicated that actually there are micro-organisms and spores of mosses and lichens in latent form, which can come alive under favorable warm and humid conditions. A more detailed study of the chemical and mechanical action of specific ruderal plants present on the fallen west gable end of the palatium is urgently needed.

Samples taken from several places of Lednica Island were examined and the latent presence of photoautotrophic micro-organisms was detected. It seems useful to study lichen and moss flora on the ruin. The results should make it possible to identify several moss and lichen communities. The ecology of each community determines the deteriorating mechanism. The knowledge of these dependencies will facilitate the selection of appropriate preventive procedures.

### Conclusion

Complex investigation and experiments provided evidence that the most suitable approach to preserving medieval relics of the Royal Castle at Lednica Island is to protect them from moisture and frost as well as to consolidate the weakened gypsum-lime mortar by means of an activated saturated solution of barium hydroxide, aluminum-magnesium-calcium silicate with the addition of catalysts.

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## Abstract

Disodium EDTA has often been mentioned in relation to the removal of crusts and for general cleaning of stone including marble. Recent research undertaken by Artcare through a grant from the Australian Institute of Aboriginal and Torres Strait Islander Studies (AIATSIS) has shown that although EDTA dissolves gypsum it has a more pronounced effect on other constituents of the stone. The current research has assessed the impact of various treatments on sandstone commonly found as the support for Aboriginal rock paintings together with crusts and pigments typically present on the surface of the stone.

## The Impact of Disodium EDTA on Stone

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### Introduction

EDTA has been recommended for a variety of treatments ranging from textiles to bronze. The following list gives some of the uses described in conservation literature.

reference	object	treatment
[1] Price		analytical procedure
[2] Bone	fresco	test removal of iron stain (not recommended on haematite)
[3] Makes	easel painting	inhibit enzyme activity
[4] Sramek	marble	tested but not recommended
[5] Rossi Manaresi	limestone	removal of unspecified crusts
[6] Alessandrini	marble	iron stain removal
[7] Rossi Manaresi	various	
[8] Stambolov	marble	iron stain removal
[9] Ganorkar	metal	advises against use on metal
[10] Carter	textile	removal of iron-based stains
[11] Matteini	bronze	corrosion removal
[12] Newton	glass	removal of mineralisation

In addition to these references the author has observed the use of EDTA on numerous fresco paintings. In many cases caution is advocated in the use of EDTA, but generally only in the application time.

This paper has studied the effects of EDTA on many common stone constituents and mineralisation surfaces that form on stone.

### The Research Project

The research has been largely funded by the Australian Institute of Aboriginal and Torres Strait Islander Studies (AIATSIS) under their Rock Art Protection Program. The research project has run for three years covering all aspects of the removal of water soluble salts and less soluble mineralisation crusts from sandstone [13,14]. Further research has been funded by the same body on the removal of iron stains [15]. This paper reports exclusively on the results of the research into the removal of mineralisation surfaces. Although the research has studied painted sandstone the findings are relevant to all stone.

EDTA has been chosen as a focal point due to its common application to many objects, but other reagents, taken from the literature, have also been studied in combination with the various components of rock art surfaces.

### Research Objectives

The objective of the funded research has been to develop methods for the removal of mineral surfaces forming over and obscuring rock paintings. Each of the recommended methods has been assessed not only for their ability to remove the mineralisation but also for the impact they may have on the stone, pigments and tenable surfaces. The removal of mineral surfaces has received varying degrees of study ranging from gypsum having a wide literature coverage to oxalates with virtually none.

### Research Methods

A wide range of experimental data has been gathered for the removal of salts, but this paper concentrates on the solubility series carried out to determine the

solubility of water insoluble minerals. The following reagents and minerals have been studied:

Mineral	formula	key = Binder Crust Pigment on rock art		
		B	C	P
calcite	$\text{CaCO}_3$	B	C	P
gypsum	$\text{CaSO}_4 \cdot 2\text{H}_2\text{O}$	B		P?
quartz	$\text{SiO}_2$	B	C	
whewellite	$\text{Ca}(\text{COO})_2 \cdot \text{H}_2\text{O}$		C	P?
haematite	$\text{Fe}_2\text{O}_3$	B	C?	P
kaolinite	$\text{Al}_2\text{O}_3 \cdot 2\text{SiO}_2 \cdot 2\text{H}_2\text{O}$	B		P
yellow ochre	$\text{Fe}_2\text{O}_3 \cdot \text{H}_2\text{O}$	B		P
red earth	$\text{Fe}_2\text{O}_3$	B		P
rust	Fe compounds	B	C	

The samples used were pigment quality minerals or laboratory grade chemicals as appropriate. Their purity from macro-contamination was checked in each case using a Polarising Light Microscope.

Reagent	Formula	Merck	
		no.	pH
distilled water	$\text{H}_2\text{O}$	9853	5.5
AB 57	[as per ref. 16]		8.5
ammonium carbamate	$\text{NH}_2\text{-COONH}_4$	518	8.5
di-sodium EDTA	$\text{C}_{10}\text{H}_{14}\text{N}_2\text{Na}_2\text{O}_8$	3487	4
tetra-sodium EDTA	$(\text{NaOOCCH}_2)_2\text{NCH}_2\text{CH}_2\text{N-}(\text{CH}_2\text{COONa})_2$	3488	11
sodium hydroxide	$\text{NaOH}$	8462	13
potassium acetate	$\text{C}_2\text{H}_3\text{KO}_2$	7474	7
sodium citrate	$\text{C}_6\text{H}_5\text{Na}_3\text{O}_7$	8435	8
potassium carbonate	$\text{K}_2\text{CO}_3$	7493	12
ammonium thioglycollate	$\text{HS} \cdot \text{CH}_2\text{COONH}_4$	?	8
thioglycollic acid	$\text{C}_2\text{H}_4\text{O}_2\text{S}$	9176	9

The reagents were all prepared as 5% solutions in distilled water. 10g of solute were held in a Nalgene filter funnel with a  $0.45\mu\text{m}$  mesh opening. 100mL of the reagent was applied to each filter funnel and left for timed intervals. For each reading the reagent was drawn through the funnel and the remaining weight recorded. The same reagent was re-applied to the solute and left for the next reading period.

Readings were taken at intervals up to 135 days although this was modified in some cases, especially where results were not becoming significant with time. The graphs have been confined to the first 28 days' readings. The results were entered into a computer spreadsheet and graphed. Observations of the developing graphs helped determine the length of each test where no solubility was detected.

### Results of the Solubility Series

The results of the research have revealed some important findings for the treatment of mineralisation surfaces on objects. The most important finding, and one that has been alluded to previously [2,4,9] is that disodium EDTA is quite an aggressive reagent for calcite.

Following the literature the author had applied disodium EDTA to a rust stain on a marble fountain. Contrary to expectations the EDTA had little effect on the rust, but had clearly etched the marble.

The following sections summarise the results of the solubility series:

### Disodium EDTA

EDTA has six negative sites, two nitrogen atoms with lone pairs and four carboxylic acid groups. These negative sites can attract positive metal ions and surround and hold them. A metal ion has a coordination number, which is the



number of bonds it can form, i.e. Cu 4, Fe 6. In solution there is competition between the metal ion and hydrogen ions for the negative sites.

pH plays an important role because in acid solutions the hydrogen ions on the carboxylic acid groups stay attached, providing fewer sites for the metal ion and thus reducing the chelating power.

If the hydrogens are replaced with sodium there are less hydrogen ions with a consequent pH increase and the sodium atoms dissociate in solution more readily. Disodium EDTA, as its name suggests has two sodium substitutions whereas the tetra- form has one sodium on each acid group. This explains the higher pH of 4-EDTA.

In titration chemistry the free metal ions react with the EDTA but it has yet to be explained whether EDTA can more readily remove an ion from a crystal lattice than an acid of similar pH. The graph of the solvent action of disodium EDTA shows many points of interest (figure 1).

Firstly, it clearly shows that 2-Na EDTA is more selective for calcite than for gypsum.

There is a mass increase in the gypsum funnel and this was manifested in the growth of very large crystals. This treatment cannot be recommended for the removal of gypsum for three reasons:

1. It is less efficient than ammonium carbonate or AB 57 (figure 3) and dissolves calcite more readily.
2. Stone containing a calcite binder would be seriously affected by this treatment.
3. The increase in mass of the gypsum combined with visible crystal growth in the buchner funnel suggests that this reagent deposits undesirable minerals in the stone. This is discussed further in a later section.

In conclusion it can be stated that disodium EDTA should be used with great caution when applied to calcareous objects. Figure 1 supports the observation at the Rupertswood Fountain that di-sodium EDTA is an aggressive agent for calcite. There are better methods for the removal of gypsum and the results for haematite and rust indicate that they also are not the best choice for this application. The fountain certainly showed that disodium EDTA was unable to remove surface rust from a Portland cement mortar used to bed the water feed pipe inside the marble stem.

### Calcite

Calcite has been identified as a mineral crust forming over paintings in limestone caves, over fresco paintings and on glass [12]. Where calcite has been removed EDTA is generally employed, although Newton urges caution due to the effects on the glass.

More important than its presence as a crust is the fact that calcite is common to the structural integrity of marble, limestone and many sandstones and for this reason treatments for the removal of crusts have been tested for their impact on calcite.

Figure 2 shows the solubility graph for calcite.

It can be seen from this graph that the two EDTA reagents dissolve calcite quite markedly. They may be desirable for the removal of calcite but should be used cautiously where calcium dissolution is undesirable. Reagents can be confined to the surface by carefully designed poultices.

Treatments that have minimal impact on calcite include distilled water, ammonium carbamate, sodium hydroxide and AB57. During the solubility research it was noted that many of the funnels containing insoluble minerals showed weight gains where sodium reagents were present. Further preliminary research has been carried out to determine the extent of residual sodium from various treatments and this is discussed in a later section.

Thioglycolic acid or ammonium thioglycollate are preferred for the removal of iron stains from calcite [8,15]. The reconversion of sulphated marble has been



Figure 1. Solvent action of disodium EDTA

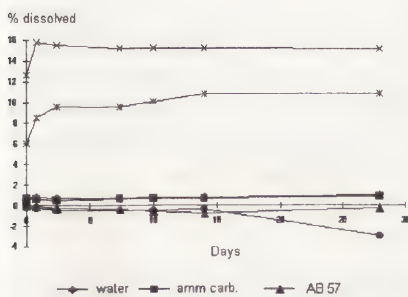


Figure 2. Solubility of calcite

advocated [17,18] and this may be the preferred treatment although it must be borne in mind that the reconverted carbonate may well turn to sulphate again. In this case the treatment cannot be considered an effective long-term strategy.

### Gypsum

Gypsum forms on many rock types and has been described extensively in the literature. Most commonly it has been described on sandstone, marble and limestone, but in Australia it is also found on granite [19]. Minarik et al [20], in identifying a Bohemian granite have indicated the presence of Ca as 1.36% CaO that is readily dissolved from the surface of the granite and free to combine with atmospheric sulphur.

Sulphate levels measured in rain in Australia range from 4–152  $\mu\text{eq/L}$  and in fog waters from 19–59  $\mu\text{eq/L}$  [21]. Equivalent values in more polluted areas of the northern hemisphere are 30–102 and over 5,000  $\mu\text{eq/L}$  respectively [22].

Figure 3 graphs the results of the solubility series.

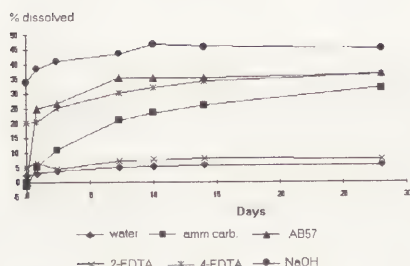


Figure 3. Solubility of gypsum

It can be seen from figure 3 that sodium hydroxide is the most aggressive reagent for gypsum. During the research NaOH was not considered as an appropriate reagent for the treatment of stone but was included in the solubility series after work by the author at a rock art site in California [23] where NaOH was tested to remove graffiti from a gypsum encrusted sandstone. The resultant surface had changed from a typically black gypsum to a contrasting white form. The effects of sodium hydroxide will be discussed further.

Of significance in the graph is the limited effect of disodium EDTA (2-EDTA). Tetra-sodium EDTA, ammonium carbamate and AB57 have all had a pronounced effect. Tetra-sodium EDTA (4-EDTA) is not recommended where gypsum has formed over calcite as figures 1 and 2 demonstrate. These graphs show that EDTA has a marked effect on calcite.

The author confers with Sramek that ammonium carbamate is the preferred choice for gypsum removal. Although figure 3 shows it to be the fourth most effective reagent for gypsum, it is the first to be sodium free and thus less likely to contaminate the stone.

Figure 4 demonstrates the selectivity of ammonium carbamate for gypsum.

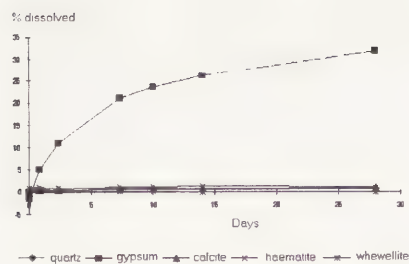


Figure 4. Solvent action of ammonium carbamate

### Quartz - Silica

Although silica has been identified as a mineralisation crust forming over rock art surfaces [24,25] and as an alteration crust on stained glass [12] this research has been concerned with the impact each reagent will have on silica in the matrix of sandstones in particular and other stones in general.

None of the reagents showed a greater solvent action than water although several showed weight gains. Of note is the weight gain observed in four of the five sodium-bearing reagents. Sodium hydroxide is the only sodium reagent that has not shown a weight gain, but this is probably due to the masking of sodium deposition by solubility of the quartz. The weight gains concur with the crystal growths in each of the buchner funnels and are discussed further.

### Whewellite

The calcium oxalates Whewellite and Weddelite have received much attention in recent years and their formation mechanisms have been well expounded. Conversely very little attention has been devoted to the removal of oxalates, although their presence on the Ghirlandaio frescoes [26] was considered undesirable because it was "practically impossible to eliminate directly since it is affected only by extremely aggressive reagents."

In Australia the presence of whewellite on rock art surfaces has become a common occurrence [25] found abundantly in tropical areas, not only on painted surfaces but those with no cultural activity or occupation evidence. Generally oxalates are found forming over gypsum layers.



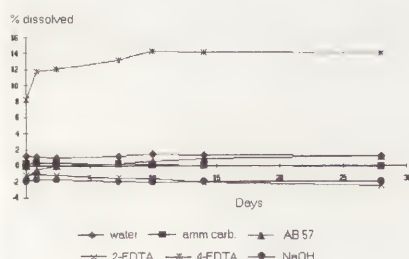


Figure 5. Solubility of Whewellite

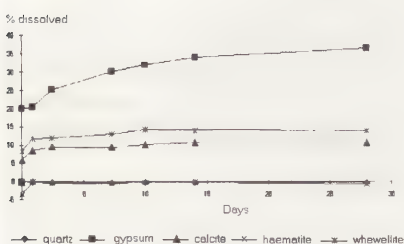


Figure 6. Solvent action of tetra-sodium EDTA

In this research whewellite has been considered solely as a tenable surface although its colour is such that it would readily obscure paintings over which it forms and alter the appearance of marble. That it has not been identified as an obscuring film is largely because the paintings become concealed very quickly.

Figure 5 shows the solubility of whewellite.

The curves indicate that tetra-sodium EDTA has a pronounced effect on whewellite while all other reagents have a minimal effect. Figure 6 indicates that 4-EDTA will dissolve gypsum more rapidly than whewellite and also dissolves calcite to some extent. Tetra-sodium EDTA is therefore not a particularly selective reagent but one that could be useful in some applications. On a fresco where 2-EDTA has been employed with safety, the findings of figure 2 suggest that 4-EDTA would have less impact on the fresco. Furthermore the 4-EDTA should be able to remove oxalates effectively as well as any underlying gypsum films.

Tetra-sodium EDTA has seldom been mentioned in the literature although it has been advocated in combination with disodium EDTA (the combination referred to in the text as Trisodium EDTA[11]) for the removal of corrosion from bronze. Mixtures of di- and tetra-EDTA offer the advantage of pH control in the range 4–11 and have been used by Artcare for experimental carbonate removal on outdoor lead statuary.

### Haematite, Kaolinite, Yellow Ochre, Red Earth

These materials have been tested and all are stable to the reagents tested. They have all been categorised in the research materials section as both stone constituents and pigments. Further testing is currently being undertaken on painted out samples of all the pigment minerals to measure colour changes.

### Rust Stains

Again the research in this area is incomplete. Initial results indicate that 2-EDTA is not an ideal reagent for rust, particularly where it occurs on calcitic stones. The example of the Rupertswood fountain has served as sufficient testament for the avoidance of 2-EDTA for removing iron stains from marble. Initial tests for effective removal of iron stains indicate that the best two treatments are thioglycollic acid and ammonium thioglycollate. Both are effective over a wide pH range and have been employed during concurrent research at pH 9 successfully [15]. The only problem with these thio compounds is that the Fe complex turns violet before fading away. This is only a short-term problem but one that needs to be understood by the conservator and curator during treatment.

### Sodium Deposition by Selected Reagents

Where sodium-based reagents were applied to insoluble minerals, particularly quartz, there was a noticeable weight gain. This could only be explained as the growth of hydrated sodium salts although no analysis of the species was undertaken. This observation, which was most pronounced in the AB57 funnels, prompted a further investigation of the sodium deposition of that particular reagent. Other sources of sodium such as sodium-modified cellulose and clays were also tested as these have been suggested as a medium for poultices[27]. All of the sodium reagents are currently being assessed to complete this research.

To test the deposition of sodium, test blocks of dental plaster were made up with distilled water and the reagents applied as 5% solutions in poultices containing 3% methyl hydroxyethyl cellulose. The sodium cellulose was tested in place of the MHC.

The poultices were applied to the gypsum blocks for 20 hours. Once the poultice was removed, the surface was washed and the blocks allowed to dry for 5 days. Dryness was confirmed using a moisture meter. This application method was considered typical of a normal site application.

After the five days the samples were then immersed in distilled water for a

further 20 hours to extract any soluble minerals. The water extracts were then submitted for quantitative sodium analysis using Flame Atomic Absorption Spectroscopy. A blank containing only the distilled water applied to gypsum was also run. The preliminary results are outlined below.

Sample	Na (gm m <sup>-3</sup> )
gypsum block (control)	22
Paper pulp	21
Bentonite	18
Tixogel WM	16
Ball clay	15
AB-57	565
Na CMC	56

These results are only preliminary and have been run on only one sample so cannot be considered scientifically reliable. However the figures themselves do show some consistency in that the sodium-containing clays do not release sodium into the block but remain consistently close to the sodium levels found in the gypsum block itself.

Of most interest however is the fact that the AB57 that had developed large crystals in the quartz solubility tests released an enormous amount of sodium. It is also notable that sodium-modified cellulose ethers also release sodium in solution.

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### Abstract

Water leaking through roof tiles during heavy rain causes severe problems to the structure of Pranakornkiri Palace in Thailand. This paper deals with efficiency tests of different water-repellent agents on the tile material. These agents have been used for almost 30 years for the impregnation of European and American sandstone and limestone buildings. Moreover, durability of the treated samples is tested in long-term climatic changes.

### Keywords

Hydrophobic, water repellent, roof tile, impregnation, Thailand

## Hydrophobic Treatment of Roof Tiles from Pranakornkiri Palace/Thailand

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### Introduction

Until now scientific tests have never been conducted to find suitable chemicals for the conservation and restoration of ancient building materials in Thailand. Often the original ancient materials were pulled down and replaced by new materials.

A scientific case study was undertaken to find suitable water repellents for impregnating old roof tiles at Pranakornkiri Palace, both to conserve them and to contribute to future conservation treatments. Two pieces of roof tiles from the palace were available on which to investigate the material parameters and to carry out impregnation tests with different hydrophobic agents.

### Historical Background and Material [1]

The Pranakornkiri Palace is situated in Petbury Province which is about 150 kilometers south-west of Bangkok. It was the first palace in Thailand to be built on a mountain, rising 95 meters above the sea, with magnificent palace structures and religious buildings beautifully fit into the natural surroundings of wood, rocks and caverns. It was constructed by King Rama IV in 1859. Owing to the King's great interest in western knowledge and culture, the palace buildings were influenced by western Neo-classical architectural style, as well as Chinese workmanship in such details as the roof structures and roof layings. The resulting palace is an interesting hybrid of architectural styles.

In the past, it was used as a vacation palace by members of the royal family, for holding royal ceremonies, and as a guest house for head of state visitors. At present, it is a valuable landmark for the study of art and history, and has become the prime tourist attraction of the province.

The palace structures are built of wood, brick and plaster. They have gradually become deteriorated over the years, and renovation began in 1982. One of the deterioration problems is a leaking roof due to high water absorption of the tiles, which causes rain water to penetrate into the buildings. The roof tiles are Chinese in style; while they are old, their texture is still in good condition.

The roof tiles are rectangular and concave in shape and some 6–8 inches in size (Fig. 1). From thin-section microscopic analysis, it can be seen that some 70% of the material is clay, 20% consists of endogenous material (5% lapilli and 15% vitreous compounds), and the remaining 10% is quartz. Organic material is not detectable. In the X-ray diffraction pattern, quartz is found to be the only crystalline component. TG/DTA measurements show that the material has been fired at very low temperatures.

### Methods

Successive experiments were carried out as follows:

The water absorption of the untreated tile samples was measured on different positions of the sample by means of Karsten Testing tubes. By this non-destructive method, the coefficient of capillary water absorption can be calculated [2].



Fig. 1. Chinese-style Roof Tiles at Pranakornkiri Palace

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A drillcore slice was taken from each sample, and the overall water absorption was measured by the mass gained after storing the samples under water for 24 hours.

After drying, the water vapour permeability of the same samples was estimated by the “wet-cup” method [3].

After the impregnation treatment, these parameters were determined again and compared to the untreated material.

Treatment

For impregnation, four different Si-organic agents were used that are very well known in Europe (Tab.1). Additionally, one of these agents was tested in different dilutions of toluene.

Table 1. Impregnation of tiles—Pranakornkiri Palace/Thailand. Treatment by capillary absorption.

Sample	Agent	Chem. comp.	Area [cm <sup>2</sup> ]	Time [min]	kg/m <sup>2</sup>
PKK 1-1	W 090 S	Olig. methyl siloxane	131	2:30	0.53
PKK 1-2	W 190 S	Isooctyl polysiloxane	115	1:40	0.43
PKK 1-3	W 290 S	Olig. isooctyl siloxane	118	2:00	0.68
PKK 1-4	W-H	Silicic acid ester + olig. isooctyl siloxane	122	1:10	0.66
PKK 2-1	W 190 S	s. 1-2	113	3:25	0.59
PKK 2-2	W 190 S	Dilution 50% in toluene	107	3:35	0.93
PKK 2-3	W 190 S	Dilution 25% in toluene	109	2:35	1.07

The tile samples were stored at 22°C/75% RH, which roughly corresponds to the average wet conditions in Thailand. After 10 days, each sample was divided into 4 segments and treated drop-by-drop with a laboratory spray bottle, while monitoring the uptake of the agent and the application time (Tab.1). The treatment was stopped when the pore space was filled and the agent ran off.

In addition, the two drillcore slices (DCS) were treated by storing them in the agents for 10 minutes (Tab.2). In this way, the maximum efficiency could be determined from two of the agents.

Table 2. Impregnation of tiles—Pranakornkiri Palace/Thailand. Treatment by storing under agent.

Sample	Water absorption* (m%)	Agent	Agent absorption (m%)
DCS 1	16.1	W-H	13.6
DCS 2	13.7	W 190 S	13.1

\* Measured by 24 h of storing under water.

Results

Water Absorption

Table 3 shows the water absorption coefficients of the untreated and the impregnated samples, derived from the Karsten tube measurements. As can be seen, there are large differences in absorbency at different positions on the untreated samples due to the inhomogeneity of the material. The water repellent efficiency of the treated material is sufficient in each case. However, there is a decrease in efficiency with rising dilutions of W 190 S. In the case of a solution diluted to 25%, the water absorption coefficient is already close to the critical value of 0.50 kg/m<sup>2</sup>h<sup>0.5</sup>, which is valid for renderings and mortars [4]. Therefore, the critical value could be exceeded by aging.

Table 3. Water absorption coefficients from Karsten measurements or water drop intrusion test.\*

Sample	w [kg/m <sup>2</sup> h <sup>0.5</sup> ], untreated	Treatment	w [kg/m <sup>2</sup> h <sup>0.5</sup> ], treated
PKK 1-1	2.64	W 090 S	0.06
PKK 1-2	2.07	W 190 S	0.06
PKK 1-3	5.82	W 290 S	0.04
PKK 1-4	4.55	W-H	0.04
DCS 1	—	W-H	<0.2*
PKK 2-1	4.58	W 190 S	0.04
PKK 2-2	4.80	W 190 S (50%)	0.07
PKK 2-3	4.72	W 190 S (25%)	0.33
DCS 2	—	W 190 S	<0.2*

Table 4. Diffusion rates i (water vapour permeability).

Sample	Treatment	Diffusion rate i (g/m <sup>2</sup> h)
PKK 1-1	W 090 S	4.84
PKK 1-2	W 190 S	5.00
PKK 1-3	W 290 S	4.36
PKK 1-4	W-H	4.78
DCS 1	untreated	7.30
DCS 1	W-H	3.42
PKK 2-1	W 190 S	4.87
PKK 2-2	W 190 S (50%)	5.08
PKK 2-3	W 190 S (25%)	5.10
DCS 2	untreated	6.30
DCS 2	W 190 S	5.24

In the case of the drillcore slices, the water absorption coefficient could not be measured by Karsten tubes. Instead, an approximate determination was made by the water drop intrusion test [5].

By storing the samples under water for 24 hours, a remarkable reduction in water absorption was observed on the treated samples, corresponding to 8.5–10.5% of the original mass gain.

#### Water Vapour Permeability

The water vapour permeability is influenced by the treatments to a varying degree, as can be seen by the diffusion rates (Tab. 4): when the permeability of the untreated material is high (series 1-1 to 1-4), a reduction of from 32–40% is found, independent of the kind of agent used. With lower permeability (series 2-1 to 2-3), the reduction is only 18–23%.

However, treatment by complete absorption of W-H (DCS 1) led to a reduction of 53%. Among the agents in the group, W-H performed differently because it is a mixture of hydrophobic siloxane and a stone strengthener on silicic acid ester basis. The resulting silica gel is deposited within the pore space, thus reducing the permeability to a great extent. On the contrary, the other agents form silicone resin films surrounding only the surface of the substrate. Thus, the reduction of permeability is lower in those cases. It can be seen that complete absorption of W 190 S (DCS 2) does not lead to a further reduction in permeability, compared to capillary treatment (PKK 1-2, 2-1, 2-2, 2-3).

Figure 2 shows the influence of the treatment on water repellency and water vapour diffusion. In most cases, an excellent impregnation is combined with a sufficient vapour transport. However, dilution of the polysiloxane W 190 S to 25% with toluene enhances the water absorption up to 0.35 kg/m<sup>2</sup>h<sup>0.5</sup>, which is not sufficient given the heavy rain in the region. On the other hand, treatment with the strengthening product W-H leads to a remarkable reduction in water vapour permeability when the agent is applied by covering the sample. Obviously, the large amount of silica gel deposited in the pore space is responsible for this effect.

#### Aging Tests

It is known that the durability of a hydrophobic treatment depends not only on the quality of application, but also on the proper combination of material and agent [6]. To investigate the durability of the treatments, two different aging tests are being carried out. One part of the samples is exposed to rapidly-changing air humidity conditions in a climate chamber. Another series is subjected to wetting and drying cycles. The water repellency is being tested over a period of some months by measuring the contact angle of a water drop. These investigations are still in progress.

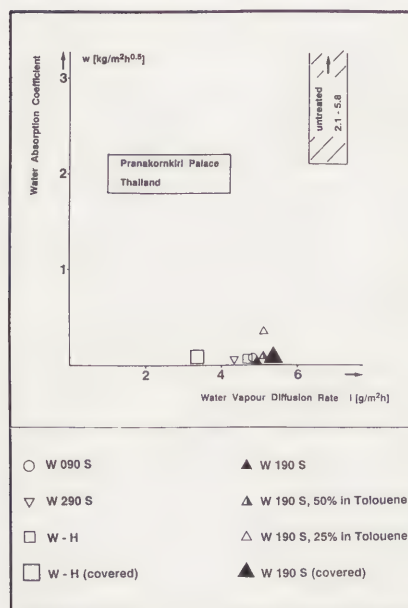


Fig. 2. Water Vapour Diffusion Rate *i* and Water Vapour Absorption Coefficient *w* of Roof Tile Material from Pranakornkiri Palace after Impregnation with Different Water Repellents



### Conclusions

Hydrophobic treatment of the roof tiles of Pranakornkiri Palace is a useful protective tool, since the water absorption of these highly absorbent materials is greatly reduced while the water vapour permeability is only slightly diminished. The use of a product that combines additional strengthening properties seems to be unnecessary since the structure of the material is in good condition. Moreover, an intensive application of this agent may reduce the water vapour permeability remarkably. A dilution of polysiloxane solutions to 25% with toluene leads to a decrease in water repellency, which is unacceptable given the climate of frequent and heavy rain. In contrast, a dilution to only 50% provides good water repellency and sufficient water vapour permeability. Thus, in economic terms, the latter treatment seems to be the most appropriate one.

### Acknowledgements

One of the authors (C. Prasartset) is a recipient of the DAAD fellowship. Thanks go to Mr. Somchart Chungsirirarak at the Fine Arts Department, Thailand, for kindly providing the tile samples.

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# Working Group II

Theory and History of Restoration

Théorie et histoire de la restauration





## Abstract

The Akans of southern Ghana believe strongly in the maintenance of their traditions through close contact with their predecessors. Therefore, certain objects, sites, and institutions that give the Akans their identity are carefully and jealously guarded and preserved; they are handed over to each generation through oral tradition, rituals, inheritance, and traditions. Some of these objects, beliefs, and practices are believed to possess the "soul" of the nation. To ensure that they maintain this identity, there are various taboos, rituals, and methods of preserving and conserving what the Akans consider essential ingredients to life. The black stool, cited as a case study, and the beliefs and conservation practices surrounding it are examined. The results of this study contribute to an understanding of conservation practices among the Akans. Even though Akan practices appear "unscientific" to many of us, these practices contain a great deal of scientific information which, if studied, can be an immense contribution towards the preservation of Akan culture.

## Keywords

Akans, conservation of African objects, black stool, sacred groves, preservation, belief, identity

## The Theory and Practice of Conservation Among the Akans of Ghana

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### Introduction

The theory and practice of conservation, of guarding important evidence of the Akans of southern Ghana and their environment, is deeply embedded in the totality of Akan life. The Akan evaluation and understanding of preservation is based on their life philosophy, which consists of both material and non-material aspects.

A study of the various beliefs and practices of conservation in Ghana—with particular reference to the Akans—shows a remarkable understanding of the value of life and nature. A careful study of the regular, unending cycle of nature, such as the rising and setting of the sun, the seasonal changes, and the rites of passage, have over the years given rise to a system of understanding and a method of sustaining this orderliness in nature by preserving what are considered to be the important components of life: the environment, values, ethics, objects, and beliefs.

Among the Akans, certain objects and sites are considered to be valuable or sacred; they provide spiritual or physical sustenance and value to life. Jokilehto writes,

Imbued with a message from the past, the historic monuments of generations of people remain to the present day as living witnesses of their age-old traditions. People are becoming more and more conscious of the unity of human values and regard ancient (objects) monuments as a common heritage. The common responsibility to safeguard them for future generations is recognised. It is our duty to hand them on in the full richness of their authenticity (1).

This paper discusses some of the methods and beliefs about conserving Akan ethnographic objects and about the environment. The black stool was chosen for a more detailed discussion because of the unique beliefs and conservation practices associated with it.

### Theory of preservation

A study of Akan conservation principles immediately indicates the problems posed by the harsh tropical climate and the prevalence of insect pests in the region. The Akan interest in history and tradition has been an age-old practice. For this reason, objects that are important and irreplaceable to them are preserved. One of Akans' main goals in preserving their culture is to maintain a link between the living and the dead, a link which is essential to their identity.

### Types of conservation

Environmental and ethnographic conservation both play vital roles in the preservation of Akan heritage.

The forefathers of the Akans realised that life would be deprived of its essential ingredients if people did not pay attention to their environment. To enforce this, various taboos, rituals, and restrictions were instituted, all of which aimed at preserving the environment. The earth is referred to as Mother Earth, *Asase Yaa*, from whom the Akan receive sustenance. They also believe in the existence of several gods. In offering prayers to the Supreme God, reference is made to *Asase Yaa* to receive the prayer, supplication, and food and drink being offered.

In the towns, certain places are reserved for specific religious reasons and for

the various spirits to inhabit. Cardinal in this principle of conservation is the declaration of sacred groves. A sacred grove is a place of restricted entry and activity. While the restrictions appear to be motivated by religious reasons, the prohibitions have also served to protect some of the rarest species of animal and plant life. Sanctions on the use of these groves for domestic activities such as hunting, felling of trees, and farming include insanity, death, or the pacification of the gods.

In almost every Akan community, there is at least one day on which a farming or hunting activity is forbidden. The abstention from these activities allows the people the opportunity to rest and the land a chance to replenish itself.

In the farming areas, it is a taboo for anyone to bring home an entire bunch of palm fruits from the farm; because any palm fruit brought home is be cooked, its kernels will not germinate when planted. It is, therefore, a matter of custom that the person harvesting palm fruit cut a bit of it off and leave it on the farm. The squirrels and crows, which feed on palm fruit, will help spread the seeds (2).

The ideas of ethnographic conservation are closely connected to Akan environmental conservation. The necessity of preserving the land and its fruits for future generations is as important as preserving the objects that carry historical and ritual significance for the Akan.

Manufactured material objects such as brass bowls, war smocks, ammunition belts, and pots are either made or bought to serve certain purposes. A war smock that was used in an expedition is kept under lock and key. It is not kept as an individual's property, but as a family treasure and as evidence of the role the forebearers have played in the town. It contains the "soul" of that family and during festive occasions, it is brought out to the public. The war smock serves as a reminder to the Akan of their ancestors and gives inspiration to the family.

Several other valuable ethnographic objects such as brass bowls, pots, and beads are handed over to members of the family as important family treasure that should be jealously guarded—for some of these objects have been acquired with blood and toil. In these instances, the objects are stored in rooms and not displayed. Some of the methods of storage include keeping the object in a box or wrapped up in cloth. The absence of ultraviolet radiation from these areas is an essential condition in preventing the objects from deteriorating. Even though, where scientific measures are concerned, the boxes and cloth used to serve as buffers are not airtight, they are nevertheless quite effective in absorbing sudden climatic changes.

There are occasions where these objects are used periodically. During such occasions, the objects are cleaned. Every form of maintenance that needs to be performed is carried out to ensure that the object remains in good condition to be handed over to the next generation. Because of the storage method and regular inspection, insect activity is reduced to a minimum.

The Akan methods of conservation vary from very simple processes, such as removal of surface dust, to very elaborate ones, as in the case of the black stool. The method of conserving the black stool is presented as a case study of Akan conservation practices.

### **The black stool**

The political organisation of the Akans revolves around the black stool, which is the "backbone" of this institution. The black stool is a sacred symbol of authority. During the installation of a chief, the new chief swears an oath to both his forebearers, who are believed to inhabit the stool, and his elders. It is, therefore, from this oath and the various rites that are performed during installation that the new chief receives his political, legal, and jural mandate to rule. During this occasion, his buttocks are lowered toward the black stool, but never touch it. It is believed that if his buttocks touch it, he will become impotent. After installation, the chief becomes a sacred person because "he sits on the stool." The stool is also believed to be the resting place and symbol of his soul and is, therefore, accorded great honour and respect (3).



The word stool refers to a wooden seat which is sometimes used to denote the office of the chief (4). Its significance is, first, as a work of art, secondly, as a utilitarian object and, thirdly, as a religious object in shrines and palaces and in the homes of families who hold certain important offices of state.

The sacredness of the position of the chief and the stool on which he sits is further emphasized by the taboos and prohibitions surrounding them. For example, a chief may not strike a person, nor be struck by anyone; he may not walk barefoot, nor may his buttocks ever be allowed to touch the ground.

A stool is made up of three parts: the base, the middle part, and the top. The base is in the form of a rectangle. The middle part has no regular shape; many different patterns, symbols, proverbs, and various representations of Akan maxims can be carved into its surface. The crescent-shaped top of the stool indicates whether the stool is male or female. For example, a zigzag decoration at the end of the four pillars that support the top indicates a male stool. The absence of supporting pillars indicates a female stool.

The decision to blacken a stool is made by the elders and performed for chiefs who exhibited good and upright qualities according to the ethical and cultural traditions of the society and who died while "sitting on the stool" (i.e., while in office). It is essential to note that it is the stool that a chief used most that is blackened after his death.

However, there are many other and varied criteria for creating black stools. In Asante, a meritorious military service, tactical manoeuvre, skillful craftsmanship, and several other reasons could merit a person's stool being blackened after his death. In Akuapem, a good performance in a social event could lead to the creation of a black stool as an expression of gratitude.

The black stool in Twi (Akan language) is called *akonnua tuntum* or *apundua*. There are a number of reasons for blackening the stools of the chiefs who the elders and the society want to honour: to preserve the stool so that it will not appear ugly; to honour its representation of the dead chief; to produce a feeling of awe and reverence in those who appear before the stool; and to make the stools durable since they will perpetually receive the sacrifices and offerings of the people (5). The colour black in Akan culture symbolises age, antiquity, tradition, and history (6). Sarpong relates that after a dead chief has been selected to be remembered, a special ceremony is performed to blacken his stool (3). Libation is poured on each of the stools of his predecessors to invoke their blessings on such an important ceremony. The spiritual aspect of blackening and the role of the ancestors must be emphasized here.

Permission is initially sought from the spirits that inhabit the tree used in carving the stool. It is from these rites that the stool then becomes a possible abode for a spirit. The rituals and religious materials used in this ceremony are very important aspects of the blackening and the conservation of black stools.

After prayers and the invocation of the ancestors, eggs are broken into an earthenware pot or a calabash and mixed with gunpowder, soot, and sheep's blood. Some of this mixture is collected and smeared all over the stool. After this process, the stool becomes a sacred religious object with taboos and prohibitions, and it is revered by the elders of the state.

On every Akwasidae, the stool rooms are visited and the stools "fed." The symbolic conservation found here is that the blood smeared on the stool contains life. By offering blood to the stool, the Akan give food and life to it as a symbolic way of preserving it. The lungs of an animal, the meat offered to the stools, symbolically give the stools breath.

### **Materials involved in a blackening ceremony**

The materials involved in a blackening ceremony include wood, gunpowder, soot, salt, and alcohol. Their role in conservation of stools is outlined in the following discussion.

Stools are carved out of wood, which is made up of cells, cellulose, hemicellulose, and lignin, containing either bound or free water. Wood has seasonal

growth and the size of the cells depends on the amount of water available during the season. Some amount of shrinkage takes place when wood is cut and this is called seasoning. If stress become sufficiently severe, the outer layers may break or become stretched without breaking. The rate at which moisture moves in wood depends on the following: the relative humidity of the surrounding air, the steepness of the moisture gradient, and the temperature of the wood (7).

The *Nyame dua* (*Alstonia boonei*) and *Ose* (*Holerrhena floribunda*) are traditionally the most commonly used trees for carving stools. The *Nyame dua* grows in swampy and damp regions of the evergreen forests of Ghana and on the forest fringes as well. It grows to a height of about 40 m and a girth of 3 m, with a narrow buttress. The soft, light wood is yellowish-white to light brown; it is fine textured, with sap and heart woods undifferentiated. It is perishable in the ground and not resistant to termites and borers unless treated with a preservative.

The *Ose* is found in Ghana. The wood is soft and uniformly white with no distinction between sap and heart wood. It is easy to work with, but it is perishable and not resistant to termites. This is considered by stool carvers to be the best white wood available (8, 9).

The gunpowder used on the stools is a mixture of sulphur, potassium nitrate, potassium chlorate, potassium perchlorate, and activated charcoal. It also contains metal oxide. Activated charcoal works similarly to soot, which attacks fungi known to destroy wood. Sulphur is also well known for its anti-fungal properties.

Soot, which is used in the blackening, is a well-known preservative containing carbon derived from smoke. Smoking occludes water and kills all bacteria in the object.

The salt in the blackening comes from blood and from the grease and sweat on the hands of the person who combines the mixture and smears it on the stool. The salt and grease create a patina resulting from the regular handling of the stool; this patina helps to protect and preserve the surface.

Alcohol, which has preservative as well as antiseptic properties, prevents the clotting of the blood in the process of blackening. The regular pouring of libation also helps check fungal attack.

### Conservation

Black stools have a historical function as memorials to dead chiefs and to the state's history. They also have an established legitimacy in the state, affirming the values attached to role and domain of the chief. Oaths are sworn to the black stool and taboos and prohibitions concerning it are strictly followed.

For this reason, careful efforts are made to conserve the stools, which is one of the primary reasons for blackening them. The discussion, although brief, of the materials used in blackening indicates that there is a scientific and a well thought-out plan of action for the conservation of the black stools. According to Western principles, most of the materials used are not appropriate materials for conservation. Soot, in itself, may accelerate oxidation. During this process of adding soot to the stool, the wood gets darker due to oxidation. However, the dark environment in which the stools are kept slows down oxidation considerably. The strong proteins in the blood that is poured on the stool harms many polar groups causing aging to the stool. In high relative humidity and temperatures, the presence of proteins can attract some microorganisms. The presence of salt and moisture can give off acidic or alkaline vapours (some may also be hygroscopic) that accelerate deterioration.

However, despite these seemingly "unscientific" methods, the elders have evolved appropriate environmental conditions and handling procedures for the preservation of the black stool. To date, the stools remain in good condition. The preservation of the stools comprises environmental and handling procedures concerned with storage, supports, light, dirt, inspection, handling and maintenance, movement of the objects, and security.



After the stools have been blackened, they are taken to "stool rooms" that have been created to serve as their resting places. These rooms are mainly constructed with "swish" (modern rooms may be constructed with cement). This material has a slow heating property and a high heat-retention level. With this material, temperatures are kept relatively cool during the day or, at least, during a greater part of it. Swish also helps stabilize temperatures when they drop at night. The maintenance of stable temperatures and relative humidity are good conditions for the conservation of wood.

The black stools are kept on different kinds of supports, such as beds and tables, and, in some instances, inside padded boxes. The beds and tables are padded with cloth or blankets, thus preventing the scratching or chipping of the stools' edges. The stools are also left in a horizontal position, which is the most stable position for the stool. The supports also keep the stools away from the dump floor and flooding.

The lack of many windows is of great advantage to conservation. Rays from the sun weaken the wood, causing expansion and contraction. Another chief effect of light on the textile is fading and a breakdown of their fibres. Hence, the stools are kept from damage that may be caused by light.

The restriction placed on persons entering the stool rooms and the limited number of openings in the rooms reduce the amount of dirt and pollution from the atmosphere, which can create conducive conditions for microorganisms to grow.

During the 44-day Akan festival (*Adae*) of venerating the ancestors and during other festivals, the stools are inspected and "fed" with blood and alcohol. The preservative qualities of these solutions have been mentioned in the discussions of salt and alcohol. Appropriate treatment is given when any deterioration or infestation is observed.

The officials who handle the black stools are known as *nkonnuasuafo*. Their positions carry as political, social and religious responsibilities, and their knowledge of traditional methods of handling are derived from years of apprenticeship and experience. Since the stools are religious and political symbols, utmost care and respect are given to them when handling them, for there could be spiritual repercussions and sanctions for mishandling.

Black stools are turned upwards on *Adae* and other festivals and venerated with prayers, food, and drinks, and then returned to their horizontal positions. In some areas, they are brought out to be ritually washed during the annual festivals, as is the case with the six blackened stools of Okuapehene.

The responsibility of security for the stools lies in the hands of the *adumfo* (security officers), who perform this duty not only as a profession but out of a calling that has strong ancestral and family linkage. To them, this is a calling and a birthright to protect the stools (10).

## Conclusion

It is very important for the museum professional to work in close collaboration with the custodians of the traditions of the Akans. The museum professional should research the Akan methods of preservation and conservation of their culture, in order not to introduce any falsity and inappropriate methods in the way their objects are stored and presented to the public. This, I believe, will go a long way in enhancing the skills of the museum professional.

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## Abstract

Information about the origin and history of the painting, *The Wedding of Peleus and Thetis*, painted by Cornelis Cornelisz. van Haarlem in 1593, proved helpful in understanding its present condition. This information was gained by comparing results of archival research with those obtained by technical examination of the painting. The examination on the object itself was very remarkable. Due to the fact that a controversy surrounded the last restoration of the painting in 1875, ideas concerning how the treatment should be carried out have been recorded. While the early conservative treatment recommendations agree with current approaches to restoration, this does not seem to have been the practical result. Such investigations allow us to trace the "profession" of the restorer in the past.

## Keywords

Cornelis Cornelisz. van Haarlem, history of restoration, treatment of easel paintings

## A Case History of Restoration, Ideas and Working Methods in 19th-Century Holland

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## Introduction

For some years it has been customary for an interdisciplinary team to carry out a preliminary investigation before performing extensive restoration treatments in the Frans Halsmuseum. Archival research provides some information about the material histories of the objects. Of course, it always remains a question whether or not it will be possible to discover the provenance of an object. However, since the nucleus of the collection in the Frans Halsmuseum consists of paintings from semi-public institutions, some information about their origins and histories can usually be found. This paper aims to show how such research can be fruitful, not only to help the restorer understand the present condition of an object, but perhaps also to gain insight into how restorers acted in the past.

## Restoration history of the painting

The subject of this article is a large painting measuring 246 × 419 cm, which depicts *The Wedding of Peleus and Thetis*, painted by Cornelis Cornelisz. van Haarlem (1562–1638) in 1593 (See fig. 1). The painting was restored between 1989 and 1991, together with a large altarpiece incorporating wings by Maarten van Heemskerck (1498–1574) and a later centre-piece depicting *The Massacre of the Innocents* painted on canvas by Cornelis Cornelisz. van Haarlem. From the end of the 16th century until the beginning of the 19th century, these paintings belonged to the city and decorated the Prinsenhof, the guest house of the city governor in Haarlem.

In 1804, the paintings were sold to the Batavian republic as part of an exchange for the return of the town hall, which the state had bought in 1800. As state property, the paintings were exhibited in the Nationale Konst-Gallery in The Hague, the forerunner of the Rijksmuseum in Amsterdam. Over a short period



Figure 1. Cornelius Cornelisz. van Haarlem, *Wedding of Peleus and Thetis*, 1593, oil on canvas, 246.5 × 419.5 cm, Haarlem, Frans Halsmuseum.

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of time, beginning in 1804 when the museum was still unsettled, the paintings were moved from one building to another. In 1805, the *Wedding* was cleaned, overpainting was removed, and new retouches were applied. This information indicates that the painting had already been treated in the Prinsenhof when it was probably also enlarged by adding a strip along the top side of the canvas.

Some years after 1808 until the last quarter of the 19th century, *The Wedding of Peleus and Thetis* was neglected. About 1822, the painting was placed in the depot of the Koninklijk Kabinet van Schilderijen, Mauritshuis, in The Hague. The painting was stowed away in the attic of the museum, exposed to poor climatic conditions, and folded (with the paint layer turned inside). This situation tells us of the lack of appreciation for 16th century history paintings, and of the poor care of the national heritage in the Netherlands in the 19th century.

During King Lodewijk Napoleon's reign in Holland from 1806 to 1810, official policy supported the arts. After the liberation in 1813, King Willem I continued this policy on a more modest scale. After 1830, one can no longer speak of an active policy and the situation became even worse when the country was ruled by a succession of dogmatic liberal governments from 1848 onward. The credo of the liberals was that there should be no state interventions in the arts. This climate led cultural goods to move rapidly out of the country, partly due to the fact that specific groups of the population had been reduced to poverty, a situation which had already begun in the 18th century.

The 1870s were a turning point in this attitude. The Catholic lawyer, Victor de Stuers, was representative of the protagonists who wanted the government to adopt a firm policy towards the arts, particularly in regards to museum policy and the preservation of monuments. In 1873, he published a polemic essay regarding the serious situation in the Netherlands in which he made recommendation about how to save the remaining artistic and historic heritage. The outcome of many debates held by the less dogmatic liberal government in 1874 was the establishment of a government commission to advise in the care of the national heritage. In 1875, de Stuers, a member of the commission, became head of the Department of Art and Science in the Ministry of Home Affairs.

Just at this moment, when ideas about state intervention in the arts were changing, the newly appointed director of the Mauritshuis discovered several paintings, including the *Wedding*, in appalling condition in the attic of the museum. A request to the minister for permission to treat and reline the state-owned painting was met with a question concerning the proposed removal of a strip previously added across the top. The restorer, W.A. Hopman, who had been associated with the so-called "Dutch method" of wax-resin lining, sent a letter to the museum director on July 19, 1875 explaining why he felt it was necessary to remove the addition. Hopman considered it impossible to remove the creases in the painting during lining without first removing the strip of different canvas attached to the top edge. He argued that the different paint layers on the strip confirmed that it was an addition. Having unofficially consulted Victor de Stuers for his opinion concerning the status of the added strip, Hopman wrote to the director on July 20, requesting a fast decision so that the painting could be rescued from its long rest on a rope net. The director then wrote to the minister, who insisted that he consult the advisory committee, so that the lining had to be postponed. In this case, one might argue that the newly realised advisory committee was a hinderance in practice. In addition, no restorer took part in the committee.

In a letter dated July 22, 1875, the museum director wrote to inform the minister that he had consented to removal of the added strip and consequently asked to resign. In a follow-up letter dated August 12, the director reported that the picture had been lined. He also questioned whether Hopman would be capable of carrying out the next stage of treatment, which involved the skilled work of retouching and reconstructing losses. Having consulted the committee, the minister replied in a letter (August 2) that contained extensive guidelines for the restoration; these guidelines provide insight into current ideas and practice. Hopman was allowed to fill and retouch the many tears and paint cracks, but without overpainting original adjacent areas. Slight damages were to be re-



touched with fine points of paint, in contrast to larger areas of damage where strokes of paint could be applied. The minister proposed employing an artist familiar with painting technique and issues of anatomy for the large reconstructions. He further advised that the painting should be framed so that the figures were left completely visible and stated that the back of the figure seated two centimeters from the left edge should align with the rim of the silver vessel below; this recommendation, in comparison to the disregarded ministerial advice for the added canvas strip, appears to have been carefully followed. Examination before the recent restoration revealed that lats had been nailed to the right and left sides of the painting to fill the frame rabbet, so that the edges of the composition virtually coincided with the inner edge of the frame. As for the instructions for retouching, according to current standards it still seemed liberally applied, particularly in the reconstruction of the badly damaged female face by the left edge which had been extensively overpainted. The many wide cracks in the darkened paint layer of the background had been retouched, apparently with the use of a medium-rich oil paint which had wrinkled and darkened. This meant that the overlap of original paint had become more obvious. Nonetheless, a glazing, rather than the recommended pointing technique, seems to have been applied.

With ministerial permission, the group of paintings which had been removed from the Prinsenhof in the early 19th century returned to Haarlem in the second decade of the 20th century. This time, they came on permanent loan to the Frans Halsmuseum where the recent restoration took place in the gallery, rather than the restoration studio, because of the paintings' large size. The museum visitors were able to watch the treatment from behind a glass wall. The restored paintings formed the focus of a small exhibition, which opened in December 1991, containing information about the treatments and research results.

#### **The 1989–91 restoration treatment**

The wax-resin lining applied by W.A. Hopman in 1875, together with a new stretcher, were both still effective and so were preserved. Sagging deformations in the canvas (notably a significant bulge in the lower part) were eliminated by keying out the stretcher under controlled relative humidity conditions. In order to raise the heavy top stretcher bar, the wooden keys were supplemented by adjustable metal clamps attached in the corner joins to the stretcher. A few millimeters expansion of the stretcher proved sufficient to eliminate the deformations.

After removing surface grime, two thick layers of severely yellowed natural resin varnish layers were removed by gently rolling swabs dipped in a solvent mixture (11:3:6 parts of isooctane, ether and ethanol, respectively) over the surface. This same mixture removed some of the dark retouches applied during the last restoration. Other retouches and overpaint which contained lead white—notably in the badly damaged figures by the left edge—were resistant to solvents, and were removed using a scalpel under the stereomicroscope. Removal of overpaint in the top right sky, applied during the last restoration, uncovered a flat area of older overpaint. The correspondence regarding the last restoration in 1875 mentions that this older overpaint was not removed for fear of damaging original paint underneath. The older overpaint now proved virtually inseparable from original paint using reasonable methods. It was therefore thinned, and the residues were integrated by retouching.

A layer of 20% dammar varnish in white spirit was brushed onto the painting to saturate the colours and to isolate subsequent restorations. The old damages had been irregularly filled with the wax-resin applied during the 1875 lining. Where necessary, the fills were locally improved using additional beeswax. Damages were retouched using glazes of dry pigment ground in MS2A (a hydrogenated polycyclohexanone resin), exploiting the red colour of the underlying original ground revealed in many damaged areas. The badly damaged faces by the left edge were reconstructed by connecting original fragments of paint. A final thin layer of 15% dammar varnish in white spirit was sprayed onto the painting; this varnish layer was to intended to impart an even,

moderate gloss and render the somewhat uneven surface texture of the damaged painting undisturbing. As in the previous restoration of 1875, the painting was reframed to show as much as possible of the composition, cropped on the left side. However, this was achieved by fitting balsa wood blocks in the frame rabbet, rather than the previous solution of nailing lats to the sides of the painting.

### Conclusion

Before this preliminary investigation of *The Wedding of Peleus and Thetis*, little was known about its history, presumably since the painting had been cared for by a number of institutions in the past. The surprising amount of information which this investigation uncovered is probably not exceptional. Interdisciplinary research carried out on a regular basis for restoration projects could prove valuable, not only to increase knowledge about the condition of an object, but also to learn about the 'anonymous' past of a restorer.

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## Abstract

The interest in the history of indigenous Russian culture, which arose in Russia in the first half of the 19th century at the time of the Napoleonic wars, was closely connected with the rise of a national consciousness. This interest was widespread in public life. Ancient heritage became a subject of interest to writers, painters, amateurs and scientists. Public interest in preserving this heritage led to the development of conservation activity during the second half of the 19th century.

## Keywords

Russia, heritage, society, culture, art, painting, literature, conservation, landscape painting

## Cultural Heritage in the Public Life of Russia in the First Half of the 19th Century

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In Russia, the second part of the 18th century was marked by great interest in the fine arts. It was not only the Tsar's official policy which stimulated development of arts and the collection of art, but also changes in public awareness had taken place. In 1757 the Academy of the Fine Arts was opened in St. Petersburg, the capital. Just before this date, auctions of fine art also commenced in this city, and these brought art within the reach of the elite and also the public.

Collecting and sale of art of the European masters were widespread in Russia. The galleries of the princes Yusupov, Sheremiyev, Demidov and Stroganov and of many other Russian noblemen were world famous. The famous Russian satirist D. Fonvisin (1) began to trade in art during the second half of the 18th century. For years he had been studying European collections and buying pictures of European artists on a wide scale. N. Radishchev, a well-known Russian writer, wrote in his article entitled "Discussions on what it means to be a son of the Fatherland" that for an "advanced" person "to clear his taste" he should "grow fond of careful study of paintings of great artists, sculpture and architectural masterpieces and also be fond of listening to music".

However, until the end of the 18th century, indigenous art and heritage were not considered on the same level as European art. Only the latter was deserving of attention and worth copying. Paintings of ancient Russian religious buildings and cathedrals were valued only for practical reasons.

The opening of the St. Petersburg Academy of Arts is considered to be the date at which indigenous fine arts were first properly recognised. The Academy was, however, also meant for copying and reproducing European fine art. The refinement of native fine art and the appearance of native artists at the end of the 18th century/beginning of the 19th century, signalled the revision of attitudes towards native art. Russian art was now being regarded in proper historical perspective. The rise of the patriotic fervour during the Napoleonic wars also contributed to this process. As late as the 1820s, articles in Russian periodicals (both general and those devoted to art) complained of the under estimation of Russian antiques. For example, the *Journal of the Fine Arts* for 1823 considered that the Russian painting school did not manifest itself in Europe because too few paintings and objects survived. The article continued that "Russia experienced a great lack of ardent investigators of ancient native monuments who would pay due attention to this subject, (and who would) reveal and, after critical survey, confirm their real antiquity". For information on native Russian art in this period, we mostly have to resort to the writings of foreigners for their opinions, and even their assumptions. Such reports are often based on probability rather than upon fact.

Trying to recover the loss, the editors of the *Journal* gave summaries on the fly-leaf not only of the complete contents, but also of the section "The Fine Arts in Russia", which they noted, "had to serve for the history of arts in Russia".

The new trends influenced the subjects which could be studied by students at the Art Academy. Classical and biblical subjects were replaced with topics from Russian history, which expressed national patriotic ideas. At the beginning of the 19th century, prince Demidov endowed funds for students who wished to devote themselves to painting national subjects. The well known Russian historian Karamzin recognized the implications of the threat of destruction of historical monuments during the Napoleonic invasion of Russia. It was not by mere chance that in 1817 he wrote in his "Notes about famous Moscow mon-

uments" that "Keen necessity to know and preserve them has arisen." His "Letters of a Russian Traveller", written in 1791, played an important role in this process. They were followed by travel notes of other authors such as: "Leisure of a Crimean Judge or the second journey to Tavrida" by P. Sumarokov (1805); "Letters of a Russian, travelling in Europe from 1802 to 1806" by D. Garichvastov (1808); "Travel from St. Petersburg to Byeloziorsk" by P. Lvov (1804) and many others. Even a "Hand-guide for use in travel between the two Imperial capitals of Russia" by I. Glushkov was published in 1801. In the latter the author described the monuments of Novgorod and remarked that they "give a good idea of the taste of the first founders of Great Novgorod".

In 1808, a group of lectures by Bolchovitynov, the future bishop of Kiev, called "Historical discussions on the antiques of the Great Novgorod" were published. In the same year J.F. Bule, a German professor, gave an introductory lecture to the history of arts course titled "On the ancient Russian painting". The implication of the title was that he had included the pre Peter-the-1st period of Russian art as fine arts. The famous Russian historian Karamzin, included in his fundamental work "The history of the Russian State" (besides chapters on military forces and trade) a special section dedicated to art. In the chapter called "Russia from the 11th to the 13th century" he stressed that as well as the foreign masters, whom the "Russian(s) tried to attract to their country", ancient Russia had its own native painters. Moreover, the writer emphasized the perfect technique of their paintings in "which freshness and lustre did not fade away during the past six or seven centuries".

After Karamzin's *The History of the Russian State* appeared, Pushkin wrote:

3000 copies of this book were sold in a month, which is the only example in our country. All of us, even women of fashion rushed to read the History of our Mother land unknown to us till that time. It was a new discovery to us. Ancient Russia seemed to be found by Karamzin as America had been discovered by Columbus.

Swinjin, a Russian painter who established the first museum of the fine arts in Russia and the magazine *The Russian Native Notes* took for his motto the words:

God and Nature inspire us not only to love our Mother country but also to learn and know it—that is the Dignity, the Debt and the Honour.

V. Grigarovich, the editor of the *Journal of the Fine Arts* and an art critic, stated that "since the 1812 war for the Motherland influenced the minds of the people. Everything native, truly Russian, became more valuable even in the opinion of connoisseurs of foreign art".

It was during this process of the restoration of the status of native Russian arts, together with the revival of the national patriotic images, that the comprehension of the necessity of preserving the national heritage came into the public consciousness (2).

In the final quarter of the 19th century the school of so-called "view-painters" was formed. They were inspired by the growing interest in the native country and in the history of its culture. At that time, painters studied not only in Italy, (where the best pupils were sent on bursaries or pensions) they were often sent to travel throughout their native country. The condition for their travel was:

all you see, draw and paint should be pictured with precise accuracy as it is in nature. So you should not neglect or omit any detail which may seem to be needless, especially in copying any inscriptions or samples of art, how ever inaccurate or carelessly finished they were in your opinion (3).

It is not a mere chance that one of the well-known Russian "view-painters" of the first half of the 19th century Silvester Shchedrin wrote from Rome during his stay in 1819, "The Coliseum has ordered me to paint its portrait".

It is from the pictures of these "view-painters" whose paintings may be considered "portraits" of cities, towns, estates, buildings and separate monuments, that the outward appearance of that destroyed, ruined and reconstructed world has survived.



Rich Russian magnates used to take painters to accompany them on their journeys. Often the painters made whole albums of drawings and pictures of the places they visited for their magnates.

For example, E. Korneev, a Russian painter of the 18th century, travelled with Tatischev in Greece and Italy. In addition Borisov, on a pension from the Academy, visited the Simbirsk district with Sologub.

In the first quarter of the 19th century several albums of journeys (such as the album "A Journey from Moscow to China" by A. Martynov or albums of lithographs of Moscow sights etc.) were published. Old architecture, sculpture and painting were presented in them with precision and care. In particular, Sazhin, an academician of painting in Kiev, created for the Governor-General, D. Bibikov, an album of antiques discovered during the period of Bibikov's government in Kiev. Pictures of the exteriors and interiors of the most ancient monuments of the 11th and 12th centuries, such as the Kiev Cathedral of St. Sophia and the gold-cupolated monastery of St. Michael, were displayed in it.

The availability of various private albums shows the great interest in heritage in Russian society at that time. Among the intelligentsia of the Russian nobility, the skills of drawing and painting were as obligatory as was a knowledge of foreign languages or music. It is striking that almost all of the Russian writers were also skilful in drawing, and this was not without reason. Drawings of estates, gardens and sculpture can be seen even in the most amateurish albums.

Ancient heritage became the subject of the poetry of such famous Russian poets as A. Pushkin, V. Batiushkov and N. Viazemsky. It is interesting, however, that in 1816 A. Voejkov, a Russian writer, in his translation of the French book *The Gardens and skill to decorate countryside* by Delisle, introduced many additional stanzas describing the palaces, gardens and parks of the Gatchina, Peterhoff, Archangelskoje and Kuskovo.

The specific nature of Russian national fine arts was addressed in the aesthetic views of Russian romanticists and revolutionaries—decembrists.

The development of interest and the rediscovery of "unknown" monuments not only aroused interest but also posed the acute problem of their preservation. Therefore V. Batiushkov in his article "A journey to the Castle of Sourey. A letter from France to Mr. D", expressed indignation with the attitude of the French towards their heritage, "some travellers assure me that whole castles are being sold for removal and thus invaluable historical monuments are being destroyed" (4).

Grigorovich in his article called "About exposition of the pictures of the Imperial Academy of the Fine Arts" complained: "What can we expect when fifty years or a whole century will pass? Some of the pictures undoubtedly will perish". The famous Russian writer Gogol raised his voice against the squandering of national monuments discovered in archaeological excavations in Rome. The same concern for preserving the heritage, but in this case our native Russian heritage, also troubled M. Pogodin, a noted professor from Moscow University, who wrote in despair to Gogol in 1847:

Do you know the collection that belonged to Glinka? Till this time there is nobody who would like to buy it even for a hundred thousand roubles. What scoundrels are these rich men. It may be taken abroad to foreign lands.

He decided to buy this collection himself in order to attract the attention of the government to this situation and compel it to give money for this purpose. "Not to allow the collection to leave Russia at any rate". In 1839 in his article "In Foreign lands" Pogodin paid much attention to the poor state of protection of Russian monuments and their awful condition.

How many monuments had we to possess if even after numberless hostile invasions domestic fires and robberies of every kind, in spite of ignorant and neglectful treatment a great number of them has surveyed and is still in the possession of our government and private persons.

And then in the same vein of regret he continued about the monuments of

Venice, "All these palaces and other buildings look neglected, abandoned and deserted". In the same year an unknown author greeting the foundation of the Society of the Russian History and antiques wrote in the journal *The Russian Native Notes*:

our monuments had been ruined not only with age but also with ignorance and unwarranted diligence which often shade and even change the noble features of the past with its amendments and corrections.

F. Solntsev, an Academician of the Fine Arts Academy of Russia, showed in his work that it was not only ignorance which was a problem. Though Solntsev contributed much to the study of ancient heritage of Russia (there are some 5,000 of his watercolours devoted to this topic), on becoming a restorer he did not so much preserve the ancient paintings he treated, but rather renewed them. When in charge of the conservation work for a unique monument of ancient Russia—the Kiev Cathedral of St. Sophia—Solntsev actually falsified its 11th century frescoes in the process of restoring them. N. Ivanchin-Pisarev, a Russian writer, who was terrified by the tendency to repaint old icons, clearly expressed his attitude towards this in his book *An Evening at the monastery, of St. Simon*. He wrote "To paint a new or to renew a painting—these are two quite different arts".

The same opinion was expressed by A. Labensky, the custodian of the Hermitage. In regard to the paintings bought in Venice in 1843 he considered it necessary to warn that:

When buying pictures abroad it is necessary to make sure that they were not repainted and especially that they were not cleaned by an unpractised hand as it often happens because of unwarranted diligence of their sellers, since pictures of famous painters lose much of their merits and virtues due to these procedures.

For these reasons, Labensky included the position of a restorer working under his personal control, in the staff of the Hermitage. Russians travelling in Europe at that time closely observed the quality of restoration work on monuments. A. Tolstoy, a well-known Russian poet, described the reconstruction work of the ancient statues of Venus and Fawn by Michelangelo Buonarotti in his itinerary notes in 1831. In an article published in *The Russian Native Notes* in 1840 an anonymous author expressed his delight not so much in the actual reconstruction of Athenian antiques but with the manner of their reconstruction. Thus little by little it was not the "shining appearance of a restored monument but its similarity to the original look of the monument" that began to be appreciated. In the same journal this author also reported substantial progress in addressing the problem of preserving heritage in Russia. As a positive example, he mentioned the publication of an album of native heritage. Summing up and appraising the activity of the Society of History and Russian Antiques in revealing and preserving ancient native heritage the author of the art section of this journal concluded "if all this were published the Russian ART would get quite original appearance".

However, restoration sciences took longer to develop in Russia, and came only after much had been lost or damaged. Public opinion and Russian literature played an important role in this process.

In 1842 the following clause was included into the "Construction Regulation".

It is forbidden to start or make any renewal in ancient churches and cathedrals or similar monuments without the Imperial permission. The inner and outward appearance of churches should be preserved with assiduity, and no voluntary mending or change is permitted without consent of the ecclesiastical authorities.

Since 1843 the eparchial bishops were entrusted with the duty of supervising the process of restoration. But this principle, though positive by itself, was undermined by the lack of education and ignorance of provincial clergy. The poet A. Tolstoy wrote thus:



When church deans were asked on what grounds all the destructions and mutilations were being made they- answered with pride that there was nothing to regret because "that one was old".

The aspirations of the cultural elite and the Russian public (the real connoisseurs of art), which led to the renewed appreciation of native fine arts, also stimulated the appearance of a new generation of restorers. This new generation strove to reconstruct the original appearance of art, artifacts and monuments they restored. In particular, the restoration of paintings from the Kremlin Cathedral of the Assumption in the early 1850s was welcomed as a new epoch in native restoration since "the former restorers of ancient icons repainted them and thus spoiled them". Thus, the revaluation of ancient Russian heritage and its re-attribution as high culture, stimulated further changes in attitude towards restoration and preservation. Even though the new approach was in its infancy, restorers removed old dried oil, replaced or filled the destroyed sections and repainted them in accordance with the ancient manner. This approach meant the restoration of the original and not merely repainting. The public wished to see restored works in an authentic condition in which the originality and true character of the work could be appreciated for its real value. They did not wish to see forgeries. Public activity in supporting the restoration and preservation of the cultural heritage was reflected in the work of all those cultural workers who respected and valued their native art. These workers were not only members of the nobility, as had been the situation at the beginning of the century, but also included the so called "raznochintsy", who belonged to the lower middle class intelligentsia.

Such a man was I. Sniegirev. Though not a professional historian (he was a Latin teacher and a censor), he studied the ancient heritage of Moscow. Early in 1834 his work dedicated to Russian painting appeared. It was in this work that Russian iconography was first presented as a source of understanding or interpretation of native history. In 1843 Sniegirev also initiated a Museum of Russian Antiques.

In 1849 the book by I. Sakharov *Investigation of the Russian Art of Icon painting* appeared. Sakharov was a physician and a collector of Russian antiques. In this book Sakharov expressed doubts about the quality of icon restoration which he felt misrepresented the original image and therefore confused the attribution. He wrote, "Didn't we take the poor repainting by a village house-painter for the creation of a real artist?". Though transformed beyond recognition by all kinds of additions and repaintings so that the original genuine painting was almost inaccessible, Sakharov and Sniegirev with Podkluchnikov, a restorer, still managed to discern behind all the repairs and additions the real wealth and beauty of icons. Such investigations served as incentives for the collection of icons, not only by old-believers who had not accepted the Nikon's church reformation in the 17th century, and who had been preserving all the icons that were ordered destroyed, but also by the nobility and intelligentsia.

The professional training of restorers began in the first quarter of the 19th century. At that time, (1807), the magazine *A periodical information on useful improvements in arts, the fine arts crafts, in the most important branches of agriculture and trade* appeared. In addition to the objectives given in the title it also aimed to render practical assistance to heritage "Reconstructors".

In the foreward to the first issue of this publication, the editors declared their intention to acquaint painters with the subjects which formed the basis of complex restoration, i.e. with "sciences that are in indissoluble connections with their art". Articles that were published in the magazine demonstrated not only an interest in heritage but also a close acquaintance with them. Thus in the article "On encaustic painting and the means used for that kind of art restoration during a certain period of time with careful consideration of the way to preserve the painting technique named fresco", merits and demerits of painting in "fresco" and encaustic techniques were shown. The author of the article wrote:

... It (a fresco) cannot stand air changes and the longer sustains it these changes the more it fades and becomes pale and in the end it presents only some dark colourlessness instead of bright and lively colours. This reason

compelled restorers and scientists to seek for a remedy to preserve this sort of painting against the age attack.

In another article "On dyeing nut-wood in imitation mahogany" the problem of creation of imitative materials was given careful consideration.

In 1817 a school of restoration under the guidance of A. Mitrochin, the only Hermitage restorer, was attached to the Hermitage following the wishes of Labensky.

In the early 1820s, drawing schools were opened under the trusteeship of Stroganov, head of the Moscow school district. In these schools artisans (including those in the employ of Count Stroganov) could further their studies. Stroganov, who was also the Chairman of the Society of History and Antiques and also the founder of the Archaeological Committee, was himself a gatherer of ancient icons and had a splendid collection. He undoubtedly felt the need for his own restorers, properly trained at special schools.

In the 1820s important finds were discovered in the South of Russia. These excited and fascinated the Russian writers K. Batiushkov, A. Gribojedov and A. Pushkin, who visited the excavation sites in Olvia, Feodosia and Kerch. At that time the problem of the foundation of a national museum of history and arts in Russia became particularly acute. Between 1830 and 1840 this issue was being widely discussed in Russian journals.

In 1830, A. Venevitinov, a Russian poet, S. Shevyrev, a professor of Moscow University and the Princess Z. Volkonskaja developed a project to create an aesthetic museum of sculpture at the Moscow University. In this museum copies of the best monuments of the art world were to have been collected. In that way they attempted to compensate for the lack of sculpture at the Hermitage, which was a bulwark of the fine arts in Russia at the second half of the 18th and the first half of the 19th century. It was significant that Sviejin in his book *The sights of St. Petersburg and its environs (1816-1828)* gave a full description of the entire Hermitage. Although the Hermitage was a part of the Tsar's palace during the first half of the 19th century, it was not only students but also members of the public interested in the arts who received entrance tickets. The Hermitage was the place which formed artistic taste. Only there could Pushkin see Rembrandt's paintings. It was Rembrandt's image of an old woman which influenced Pushkin so much in his poem "A Little House in Colomna". The habitués of the Hermitage tried to exercise all their influence to convert it into a public museum. It should be recognised that though the new exhibits in the Hermitage reflected mostly the tastes of the élite, they also profoundly influenced the tastes of wider sections of society. Even the purchase of old masters depended very much on the Imperial taste or sometimes even on the international situation. For this reason a great interest in Spain and its culture arose during the Napoleonic campaign and this reached its highest level at the period of Riego's insurrection and the Carlist movement. Thus it does not require much speculation to relate Pushkin's "Stone Guest" and M. Glinka's "Jote Akagonesse" to works acquired at that time for the Hermitage's Spanish collection.

V. Levinson-Lessing, a European art critic, in his *History of the Hermitage collection* wrote that the state of the society, its interest in world cultural history and in native cultural history in particular, experienced by all strata of the Russian society, determined the status of heritage in Russian literature of the 19th century. Most importantly, the evaluation and re-evaluation of heritage made the public consider its survival. In 1831, Gogol in his "Arabesques" as well as in the articles "Sculpture, painting and music" and "On architecture of our days" gave an in-depth analysis of the origin and functions of all branches and kinds of art. In these articles the thought which served as the basis for the restoration of fine arts and heritage in the 20th century was proclaimed for the first time. Gogol wrote:

A peculiar thought used to come to my mind in former times. I thought that it would be rather useful to have such a street in our city which could include the whole chronicle of architecture. This street would in a certain respect serve the history of our taste development.



Some time later, in 1838, after admiring the monuments of Rome, he wrote in a letter "It is beautiful already for the fact that its one half presents the heathen century and the other breathes of the Christian spirit".

There is no reason, of course, to consider that Gogol advocated particular techniques for preservation of the heritage. There is no doubt, however, that his approach to the comprehension of the heritage and preservation of its various stages of development reflected a new comprehension of past cultures. This concept is one that had been developed in the minds of the best representatives of Russian thought.

### Notes

1. This trade house, shared with Closterman, a German merchant, was opened in St. Petersburg.
2. The national liberation movement sponsored the revival of interest in ancient monuments at the beginning of the 19th century and therefore positively contributed to the further development of Russian culture. It was contaminated with slavophilism which played a negative role later.
3. The order of the president of the St. Petersburg Academy of the fine arts to the painter Tichonov M. (1817).
4. The dwelling in question was Voltaire's house.

### Bibliography

An extensive bibliography in Russian is available from the author.

## Abstract

The author draws upon his work in Brazil and interviews with professionals there to trace the history of art conservation and restoration in that country. Brazil possesses vast cultural holdings, spanning the Colonial (1500–1822), Imperial (1822–1889) and Republican (1890 to present) periods. The art restoration and conservation movement in Brazil originated with the work of Edson Motta, an American-trained Brazilian, who introduced modern methods and dominated the field in his native country for more than three decades. Motta created a movement that overcame the geographic, cultural, and linguistic isolation of Brazil from the rest of the world. A phenomenal growth in national and regional academic programs and facilities that have trained restorers has, unfortunately, coincided with severe national economic problems which have limited the movement's continued progress.

## Keywords

Brazil, tropical and subtemperate climate, economic difficulties, training, modern methods, theories



Figure 1. Cities in Brazil that have major conservation facilities.

## Some Notes on the History of Art Restoration and Conservation in Brazil

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## Introduction

Both the cultural properties and the climate of Brazil are diverse. The fifth largest country in the world, its climate ranges from the tropical northern region of the Amazon to the subtemperate areas such as those found in the interior of southern Brazil. Its extensive cultural holdings mirror Brazil's geographical vastness. They include important and extensive holdings from the 18th century during the Colonial period, the 19th century spanning the Imperial and early Republican periods and the Modern period of the 20th century. This paper traces the history of art conservation and restoration in Brazil and includes technical notes related to its evolution (See fig. 1).

## Before 1950

The most important development in the care of Brazil's cultural property before the mid-20th century was the establishment, in 1937, of the Secretariat for the Care of Historical and Artistic National Heritage of Brazil, known as SPHAN (Secreteria de Patriomônio Histórico Artístico Nacional). SPHAN became the single most important government organ for the development of a national movement to care for the country's cultural holdings.

Not long thereafter, events occurring outside Brazil led to the momentous origin of the movement. Between 1944 and 1946, Edson Motta (1910–1981), a Brazilian, was receiving his training in art restoration in the United States. A Rockefeller Foundation Fellowship allowed Motta to study in the Restoration Department at Harvard University's Fogg Art Museum under Richard Buck, one of the most prominent art restorers in the world at that time. Motta returned to Brazil in 1947 with the techniques and theoretical approaches he learned at Harvard. Upon his return, Motta immediately began the organization of a department within SPHAN to undertake actual restoration of works of art. He would lead this department until 1976. In this position, he dominated the field of art restoration in Brazil, a phenomenal achievement over such a very long period by a single individual.

## The 1950s: introduction of modern theory

Expounding upon the theory of restoration (particularly of paintings) which he learned in the United States, Motta also taught at the School of Fine Arts at the Federal University in Rio de Janeiro. His two-semester-long course, "Theory of Painting Restoration," was offered from 1951 until 1980, unfortunately with very little modification of the theory over those three decades. At the same time, SPHAN mandated that Motta should take his work into other parts of Brazil. In his native state of Minas Geras, for example, he began the restoration of several important and beautiful 18th-century churches. In addition, he was obliged to go to Bahia to restore churches and historic structures in the capital city of Salvador.

The historic structures that Motta restored during the 1950s were important examples of the cultural legacy that the Portuguese had left Brazil. Motta, in turn, left a legacy of his own in the form of the training he provided to the people working at the restoration sites. This led to a growing interest among technicians and other individuals from areas, provinces, and states outside of Rio de Janeiro who shared in the care of the nation's cultural property. Still, Rio de Janeiro, which remained Brazil's capital through the 1950s, continued as the center of the restoration movement as Motta continued teaching at the Federal University, reinforcing the dominance of the Central Restoration Laboratory of SPHAN.



### **The 1960s: political and economic change**

In 1960, the capital of Brazil was moved from Rio de Janeiro to Brasília, deep in the interior of the nation, as part of a dramatic political and economic shift. In 1964, a coup, followed by military rule until the 1980s, triggered a number of fundamental changes in the way Brazil cared for its cultural property. Although Rio de Janeiro continued to be the cultural capital, the transfer of government to a new city began to drain the lifeblood of interest from preservation. The new government emphasized economic development through the construction of buildings, roads, and infrastructure, contributing to an increasing neglect of the cultural property of the provinces.

In 1969, three important books published in Portuguese expanded the knowledge of art conservation in Brazil: *The Restoration of Fine Arts*, *The Restoration of Flaking Paintings*, and *Restoration of Art Works at the National Museum of Fine Arts in Rio de Janeiro between 1967–1969*; Motta authored all three books. The latter publication was a chronicle of the restorations Motta carried out for the National Museum of Fine Arts. Although he worked for SPHAN, Motta was also under contract to bring that collection up to international standards for care.

### **The 1970s: growing interest in art restoration**

The 1970s brought more publishing landmarks, including publication of the first Brazilian book devoted exclusively to the problems of caring for works of art on paper. *Paper: The Problems in Conservation and Restoration* was co-authored by Motta and Maria Luiza Salgado. In 1973, SPHAN produced *The Technique of Encaustic in the Restoration of Paintings*, also co-authored by Motta and Salgado. Although Brazilians were familiar with restoration techniques that used wax, these influential publications were the first texts for the general public that detailed the restoration process. These publications were an important development in overcoming the geographic, cultural, and linguistic differences that isolated Brazil—and, consequently, its restoration movement—from the rest of the world. A further addition to the art literature available to Brazilians was Motta and Salgado's *Introduction to Beginning Painting*, published in Portuguese in 1976.

At about this time, Motta became director of the National Museum of Fine Arts in Rio de Janeiro, the most important cultural institution in Brazil. This offered a new position from which to promote the development and care of cultural properties. Motta continued to rely on the theories he had learned during his studies at Harvard, reinforced with periodic visits to the United States.

As the 1970s came to a close, a new direction in the restoration movement began to take shape. In Rio de Janeiro, Motta continued to teach his courses on the theory of restoration, primarily as they related to the Fine Arts School's training of painters, etc. However, another approach emerged in his native Minas Gerais, in the city of Belo Horizonte. There, Beatriz Coelho led a small core of individuals who believed in establishing a more formalized program of education and conservation training leading to an actual academic degree.

### **The 1980s: continued growth and reorganization**

The 1980s were probably the most dramatic decade in the growth of art conservation throughout Brazil, with the establishment of a number of major programs and laboratories. In 1980, a group of individuals meeting in Rio de Janeiro established the National Association for Brazilian Art Conservation. As part of its mandate, the group promotes the conservation of cultural properties for Brazil. Also in 1980, the national foundation Pro-Memória was established.

Pro-Memória was the brainchild of Luis Magalhães, who believed in decentralization of the functions of SPHAN. From the 1950s through the 1970s, little happened in the field of conservation that did not flow from or through Rio de Janeiro. Magalhães' program decentralized the restoration of cultural property in Brazil by designating each region of the country as a sector. (For example, Rio de Janeiro was sector number one, etc.) Each sector would have its own small laboratory and staff and its own budget to carry out restoration

projects with staff in Rio de Janeiro playing only a distant supervisory role. A symbiotic relationship between Pro-Memoria and SPHAN saw SPHAN continue as the national organization for the care of the country's historical and artistic heritage, while Pro-Memoria emphasized fund raising. Because it was a national foundation, Pro-Memoria, unlike SPHAN, was allowed to receive funds from donors and private institutions. This changed dramatically in the 1990s, when SPHAN and Pro-Memoria were consolidated into a new secretariat, Instituto Brasileiro de Patrimônio Cultural (IBPC).

CECOR, a department exclusively devoted to training art restorers, was established in Belo Horizonte by Federal University's School of Fine Arts in 1980. At first, the department offered a one-year course; later, this was expanded to a two- or three-year graduate level course of training in the restoration of paintings, sculpture, and, occasionally, paper. Unfortunately, at the beginning of this course of study in Belo Horizonte, the University in Rio de Janeiro underwent a crisis due to Motta's death in 1981. Efforts to transform his short courses into a full graduate program in painting or paper restoration were, ultimately, unsuccessful as the severe economic problems caused by very high inflation during the 1980s made such an undertaking impossible.

At the same time, the School of Fine Arts in the city of Salvador in Bahia also established a program. The course, once part of the school's career training for fine artists, consisted mainly of the restoration of paintings and polychromed sculpture. Unfortunately, this enterprise was repeatedly stopped and restarted because of a lack of money, becoming another victim of the economic problems that were particularly severe in this part of Brazil.

The number of restoration laboratories in Brazil grew steadily during the 1980s, despite economic problems. Several were founded, including the laboratory of the National Museum of Fine Arts in Rio de Janeiro, the Museum of Contemporary Art, University of São Paulo (founded in 1983), and the Museum of Art of Bahia; another, established in the city of Belém at the mouth of the Amazon in 1982, was a painting restoration laboratory at a municipal museum. The first of its kind in the Amazon region, this important laboratory, operated by individuals trained in Rio de Janeiro, was exclusively devoted to the restoration of paintings. In 1984, the regional Nabuco Foundation established a restoration laboratory in the northern Brazilian city of Recife. Primarily devoted to the care of books and paper and, later, of paintings, this laboratory continues to function today and has become one of the few major regional labs operating in that part of northeastern Brazil. This laboratory has been in the forefront of caring for the cultural properties in northeastern Brazil.

While restoration progressed at the regional level, important developments also continued on the national scene. During the early 1980s, the Ministry of Justice in Brasília established a restoration department for books, manuscripts, and works of art on paper. This laboratory eventually moved to the National Press in Brasília and continues to function as one of the largest paper conservation laboratories of its kind in South America. In 1986, the National Congress in Brasília also established a department for the preservation of its documents, books, and paper artifacts. This laboratory continues to function today. In Rio de Janeiro, the National Archives have also established a large conservation facility in the old mint building.

In 1987, an American-trained Brazilian photographic restorer, Sergio Burgie, returned to Brazil to establish Infoto, an important institution whose function was to help catalog, care for, preserve, and restore photographic collections throughout Brazil. Infoto, unfortunately, is functioning only marginally today, yet another victim of the nation's severe economic problems of the past few years.

The last years of the 1980s saw a tremendous growth throughout Brazil in the establishment of small, state-funded restoration departments to care for cultural property in the form of paintings, polychromed sculpture, books, and manuscripts. In 1987, for example, the State Archives of Maranhão established a restoration department for the care of books and manuscripts. Today, there are approximately 35 restoration labs operating in Brazil.



**The 1990s: current trends**

The 1990s have been characterized by the continuation of severe economic problems in Brazil, primarily very high rates of inflation. As a consequence, budgets normally associated with restoration projects throughout the 1980s are now suffering from severe cutbacks and even the closing of many labs, rather than continued growth. This is unfortunate at a time when the number of private restoration laboratories and individuals trained in the field has shifted dramatically upward. The exception to this case has been the establishment of a painting conservation studio at the Sao Paulo Museum of Art in 1991.

In addition, a national technology organization (SENAI) in the state of Sao Paulo began teaching introductory courses in book binding and the restoration of works of art on paper during the early 1990s. This particular course is the first time a national organization like SENAI, funded by private industry for the training of technicians in industry, has begun teaching courses in the restoration of books.

**Conclusion**

Given the limitations that today's economic problems have placed on the progress of Brazil's restoration and conservation movement, much is owed to the pioneering work of Edson Motta. The fact that such a far-reaching network of government programs, academic offerings, and trained personnel exists today is due in large part to Motta's dominance in the field during his lifetime. Despite recent setbacks, the past four decades of accomplishment in art restoration and conservation have left Brazil with not only an enhanced legacy of national and regional artistic treasures, but a deeper sense of value in the preservation of the cultural property Brazilians have inherited.

**Acknowledgements**

The author extends his thanks to the following individuals in Brazil who, over an 11-year period of annual visits to Brazil by the author, provided valuable contributions to this paper: Marylka Mendes, Edson Motta, Jr., Beatriz Coelho, Ana Maria de Silva, Benedicto Mello, Adelma Freitas, Marta Taveras, Ingrid Beck, Regis Concalves, Isis Baldini, Guita Mindlin, and Eneida Parreira.

## Abstract

The author considers the historical aspect of conservation of wooden statues. Concentration here is on work conducted in the 19th century and two major conservation works in the city of Kraków, Poland. Two theoretical trends represented in the last century are outlined. The author concludes that while the methods are no longer current, the knowledge about the techniques used in previous conservation work is useful in future work and research.

## Keywords

Conservation, wooden statues, 19th-century Poland

## Conservation of Wooden Sculpture in Southern Poland in the 19th Century

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## Introduction

In order to reconstruct the methods used in the restoration of wooden statues in the 19th century in Southern Poland, a region which was most active in this field, the author extensively reviewed the contemporary press and church archives relating to the two biggest conservation projects undertaken of the time: the Vit Stoss altar in the Mariacki Church and the altar of St. John the Baptist in the church of St. Florian in Kraków.

In reviewing the archives on these projects, it is evident that the contemporary conservation experts concentrated mostly on the following aspects: whether to reconstruct statues, whether to impregnate and to create a protective coating, how to perform retouching, and how to complete missing polychromy.

In relation to the problem of reconstruction, two views were common. One view is represented in "Skazówka mogąca posłużyć za przewodnik w poszukiwaniach archeologicznych" (Guidelines which could be useful as a guide in archaeological searches), published in the "Rocznik Towarzystwa Naukowego Krakowskiego," vol. XX (5), 1850. This publication was the work of the Branch of the Archaeological Association. It is written there that "if the statues are damaged and the missing pieces are lost, it is better to leave it in that damaged state than to try to complete them because the completion very often may change the object." These directives were based on the suggestions of Piotr Michałowski (1800–1855) from December 16, 1852, which were passed in 1862 by the Supervisory Committee for the restoration of the Mariacki altar: "Whatever is left of the work of the great artist should be saved untouched . . . in the state which time has kept it for us. . . . Loose pieces, however, should be carefully collected and after checking . . . they ought to be placed where a sculptor indicates." (1).

We may notice another attitude in the declaration related to the restoration of the Mariacki altar described by Józef Cholewicz and Marcina Leszczyński who write, "All sculpture should be completed by a wood-carver . . . all missing fingers and toes" (2). Józef Łepkowski (1826–1894) wrote in a similar fashion: "That which is loose (but saved) should be glued and small fragments made anew. The completion of new parts for missing ones, new gilding and painting were seen as inappropriate as the altar is to remain a treasure from the XV century and it is not the purpose here for it to look like a new work, fresh from the artist's studio . . ." (3). The authority and the arguments of Piotr Michałowski were too serious for anyone to contradict them. In this context,

The motion was carried that the work be only of a preserving nature and according to the principles which are indicated by the Hon. Michałowski. It was decided that, that which is broken (but not lost) should be glued, small missing pieces should be made anew. The whole structure of the altar should be strengthened, the statues carefully cleaned. . . . It is true that we are pleased that Michałowski did not allow for the altar to be re-gilt and varnished; it should be noted here that there is a difference between a historical museum exhibit and an altar in a church . . . it is difficult to accept that a saint can stand on an altar without a head" (4).

The second view of reconstruction was becoming stronger. The plan of Józef Brzostowski for the restoration of the altar of St. John the Baptist from 1518 in St. Florian's church in Kraków was heading clearly in the direction of complete renewal and refurbishing. It was recommended that "wherever material is completely destroyed or if by the application of special fluids the goals cannot be achieved, then they will be completely replaced by others."



Although in the beginning it was decided not to replace missing parts of the Mariacki Altar, soon this principle was changed in favour of replacing all missing parts that could be reconstructed. In consequence, under the personal supervision of Władysław Łuszczkiewicz (1828–1900) and Jan Matejko (1838–1893), Wakulski replaced missing fingers and toes, drapery, wings, etc. (5). What is more, Łuszczkiewicz also desired to complete the great Mariacki Altar with a summit of his own design. With the aim to force this idea through, he even threatened to resign from the Restoration Committee. The whole debate was settled by the conclusion of experts whose majority stated, "While at the moment no summit will be added to the altar, it will sooner or later be attempted" (6). It is likely it never came to that.

Statues from wood which were attacked and weakened by pests for a long time have been a concern to conservators of sacral objects and to museum curators.

The information which was available about the materials and techniques used for the impregnation of wooden statues in southern Poland in the 19th century indicate that the choices were wide. It was recommended that "to get rid of insects, infested wood should be treated with petroleum and it was believed that camomile placed on the wood by its smell kills worms" (7). Other suggestions were more radical: "Worms in wooden equipment and furniture may be gotten rid of when soaking the wood in copper sulphate or zinc chloride, hot flax oil or turpentine" (8). As a way for conserving wood, it was considered that to brush it several times with mercuric chloride was a very good method (1, 2). Wood was strengthened by soaking it in Indian rubber and glue and by painting the surface with hot varnish as many times as will soak into it or with hot varnish with an addition of resin (4, 9, 10). In places without polychromy, mineral oil was used to impregnate wood sometimes, with an addition of resin and a small amount of copper sulphate (4, 11). The contemporary method of using turpentine oil to soak wood was criticized: "It is not good because it can easily harm paintwork" (12). Instead, wood was impregnated on the reverse side with a mixture of turpentine oil, flax oil, a little colocynth, copper carbonate, or orpine (12). A mixture often used comprised 4 ounces (1 ounce = approximately 0.02 kg) of mastic, 0.5 ounce Venetian turpentine, 20 grams of camphor, 16 ounces of distilled turpentine oil, which was heated and melted with an addition of 20 grams of mercuric chloride (13).

To exterminate "worm pests infesting wood" and also to strengthen and protect wooden statues, it was recommended that the wood surface be covered with a mixture of varnish or soluble glass (14–16). Alternatively, the following mixture could be used: 1 pound of white colophony resin, 2 pounds of turpentine oil, and 1 drachm (0.003 kg) mercuric chloride, all melted together on a slow flame (13). A more frequently used substance was a "hot mixture of copal varnish and a small amount of turpentine oil diluted by half with varnish and flax oil"; such treatment was repeated eight times or until the shine no longer disappeared (17).

Being in the possession of many different mixtures of substances for the protection of the Mariacki Altar from insects, it was decided to paint it from the back with oil paint (minium) instead of the arduous and labour-intensive impregnation (18). The conservator, Paweł Popiel (1807–1891), using a recipe of E. Violet le Duca (1814–1879), suggested that the strengthening of small statues should be done by painting them from the reverse with litharge and varnish (19).

From a number of Kraków's 19th-century sources, a series of the most important guidelines as to the repair of damaged polychromed statues was collected. It was concluded in them that "old gold should be cleaned so as to look like new . . . while that which is very damaged ought to be replaced by new. . . . Where the polychromy is missing, it should be filled and painted . . . so as there be no difference between the old and the new colour" (2). It was also noted that "the uniformity of old parts with the fresh additions" was a concern (20).

There were also different opinions: "Conservation should only be for maintenance purposes and should not have as its aim to restore the primary freshness

of an object" (4). The two previous views of conservation work are also reflected here. The maintenance type of renovation was represented by Wojciech Eliaz (1814–1904), among others, in the program for the renovation of the altar of St. Florian. He suggested that "the renovation should be restricted to cleaning off dirt and blackened varnish and treatment of paint work and gilt only in the places which are worn and damaged, saving as much as possible of the old painting and gold work. New gilt should be covered with the appropriate fluid in order to liken it to the old" (10). How was this assessed? In the defense of repainting the statues of the Mariacki Altar, it was suggested that "it is not correct for a renovated piece to look dirty." Patination or retouching, as suggested by Eliaz, was considered to be an inappropriate method of conservation (19).

In the 1870s, the accusations aimed at the Committee for the Reconstruction of the Mariacki Altar in Krakow showed a different opinion; it was argued that too much reconstruction, repainting, and re-gilding work was done (21).

### Conclusion

The technical information mentioned here has little in common with current conservation work. However, our knowledge about the methods and materials used in the 19th century in restoration work of wood allows us to know what we may expect when conducting research or conservation work on these works of art today.

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### Abstract

The post-war years were marked by major archaeological discoveries in Middle Asia where many ancient wall-paintings as well as clay and ganch sculpture were found. These finds prompted the development of a new trend in restoration. The Hermitage Museum and the VNIIR have played a major role in saving and preserving these discoveries by developing a new conservation method which uses synthetic resins and glue. These methods have been applied by restoration specialists in Moscow, Leningrad (St. Petersburg) and Middle Asia.

### Keywords

Middle Asia, restoration, archaeology, wall painting, synthetic resins

## Parallel Progress in Restoration and Archaeology: Discovery and Restoration of Monumental Painting and Sculpture on a Loess Ground

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Progress in archaeology and restoration is closely connected all over the world, including Europe, Asia and Russia. One example of such an interaction is represented by the process of investigation and restoration used for archaeological discoveries from Middle Asia, found during the post-war period (1945–1990). This example is especially significant for the following reasons:

First, the archaeology and the restoration of art and museum valuables developed in the Middle Asia region of the former USSR during the same period as in Russia, the Ukraine and other parts of the USSR. Both developed in the 1920s–1930s and even before the October Revolution, therefore their interconnection is especially evident.

Second, the archaeology and restoration of archaeological discoveries in Soviet Middle Asia reached such a high level during the post-war era that it influenced the archaeology and the restoration of relics from ancient Russia, as well as of foreign monuments of art and culture in the entire Soviet Union.

We will not consider here the achievements of the archaeologists from Middle Asia who discovered the most ancient and previously unknown sites in the territory of the former Soviet Union, dating back to pre-agricultural civilization. These sites included settlements of the pre-Islamic civilizations of Khoresm, Sogd, Parthia, Bactria-Tokharistan with their palaces and temples, the houses and strong fortifications of rich citizens, monumental sculptures and wall paintings, art handicrafts and inscriptions in different languages.

What is important for us now is the fact that the vast archaeological study of Middle Asia by Soviet scientists from 1945–1990 not only enriched the cultural and artistic heritage of the Middle Asian peoples, but also provided a means for the rapid development of restoration techniques. These techniques have been applied to archaeological discoveries which include monumental paintings on a loess base, as well as on clay-plaster sculptures (clay-ganch sculpture). The problem of preserving such paintings and sculptures became one of the most important restoration activities at that time, not only in our country, especially in the Republics of Middle Asia, but also in many foreign states of the East.

There has been an acute necessity to develop special techniques for the restoration and conservation of wall-paintings and clay-gypsum (ganch) sculptures because of the discovery of rare paintings of this type. For example, the discovery of the ancient town of Afrasiab in Samarkand in 1913 prompted the extensive development of archaeological works in Soviet Middle Asia around that time, but neither archaeologists nor conservators could preserve the site or artifacts. The wall-paintings found in Afrasiab shrank and disintegrated soon after exposure to sunlight and air, and disappeared before the eyes of their discoverer, Y. Yiatkin. Now, the only record of these paintings that is left are coloured drawings that were made by a painter who happened to be nearby. The same fate befell the monumental paintings in Iran which were discovered by French archaeologists after the second World War. The wall paintings were excavated by the archaeologist E.G. Pchelina in 1937, at the entrance to the surface Buddhist temple at the Kara-tepe in Old Termez (South Uzbekistan). Pchelina, who had no conservation materials at hand, nor indeed any conservation experience, did the only possible thing in her power—she reburied her wonderful find.

V.A. Shishkin, an eminent man of science in the field of the protection of the ancient monuments of Uzbek, who was also a well-known archaeologist and

later a corresponding member of the Uzbek Academy of Sciences, was forced to take similar action. In 1938 he found similar paintings during the course of his investigations at the Bucharkhudats palace, at the site of the ancient town of Varaksha to the west of Buchara. It is worth noting that the careful reburial of paintings by his group preserved the Varaksha paintings for many years until such time as they could be recleaned and restored with new techniques developed by conservators at the Hermitage Museum and VNIIR scientists.

In Middle Asia during the post-war years, archaeologists began to find wall-paintings, monumental coloured-clay sculptures, and clay-gantch and gantch sculptures. The Choresm archaeological-ethnographic expedition headed by Prof. S.P. Tolstov, a famous investigator of Middle Asian peoples and history, continued the work that had been interrupted by the war. Tolstov found some samples of wall paintings on the site of the ancient town of Toprak-Kala during the first post-war field season in 1945. In 1947 he found some coloured clay bas-reliefs as well. Since that time, the discovery of wall-paintings and clay sculptures at Toprak-Kale and later at other Khorezm monument sites has become an annual event. Large squares areas of walls covered by paintings were discovered by V.A. Shishkin in 1947 during the excavation of the palace of Yaraksha. The South Turkmen expedition headed by M.E. Masson, the founder of the archaeological chair at Tashkent University and an academician of the Turkmen Academy of Sciences, came across the remains of monumental paintings and sculptures in the early stages of the excavation at the ancient towns of Old and New Nissa, near Ashkhabad. Lastly, during the Sogdijsko-Tajic expedition headed by A.J. Jakubovsky, a professor at the Leningrad State University and an eminent Russian orientalist, an excavation of the ancient town of Pendzhikent was started and beginning in 1948 new examples of monumental painting were found every year. This was the only Tajic archaeological expedition. All of these finds allowed Prof. M.M. Diakonov to state the discovery of "a sea of Sogdian paintings" at Pendzhekent. In general, the art of the old pre-Islamic Middle Asia was not ornamental. Instead it was an imitative art meant to depict precise, detailed images of items of clothing, weapons and domestic utensils.

The significance of the portraits and other paintings, as well as the carved wood and clay-ghantial sculptures discovered by the archaeologists can scarcely be exaggerated. It was not enough to excavate all these irreplaceable treasures: it was also necessary to preserve them. These splendid discoveries are a manifestation of the world's artistic culture, and are a unique source of information for studying past ages. But if humanity is in debt to the Soviet archaeologists for the discovery of these wonderful examples of pre-Islamic works of art from Middle Asia, then the recognition for their preservation belongs by right to the restoration staff of the Hermitage Museum, headed by P.I. Kostrov. These restorers developed and implemented techniques for preserving wall paintings and clay bas-relief which included the consolidation and removal of wall paintings and their transportation to restoration laboratories and workshops, as well techniques for the cleaning, consolidation and transport of charred wood. These techniques were first demonstrated at Pendzhekent and Varaksha.

Kostrov and a small group of scientific colleagues thoroughly studied the few cases in which monumental sites had previously been conserved before they proceeded to work out their own techniques. In reality, they generated a new trend in conservation science. The work of S.M. Dudin on the removal and consolidation of wall paintings from Buddhist and other religious caves and temples would serve as an example of such conservation treatment in our country. These paintings had been removed from Sinkiang in 1909-1914 during the East-Turkestan expedition headed by S.F. Oldeburg. They were saved in the Department of Eastern Culture and Art of the Hermitage Museum. These paintings were executed using the same technique as the Middle Asian paintings, except that the Sinkiang plaster included a large quantity of vegetable and animal fibres. These fibres provided stability for large sections of the paintings in the dry climate of the Sinkiang caves, and also made their removal fairly easy. Dudin simply cut ("ripped up") a large number of the wall paintings from the walls of the Sinkiang caves, and applied a light glue to the surface of the painting (a water vegetable gum) in places where the colour layer of the paintings was



beginning to peel. The back side of the removed paintings was also glued, and sometimes was even impregnated with spirit varnish. Some fragments of the Sinkiang paintings were plastered with gypsum for protection during storage or exhibition. Similar procedures were used by the German archaeological expedition to Sinkiang headed by A. Grunwedel.

Kostrov proved that, although Dudin was able to bring the wonderful discoveries of S.F. Oldenburg to St. Petersburg and even preserve them to some extent, it would be wrong to follow Dudin's example and use the same preservation techniques practised on the Middle Asian paintings found at the end of the 1940s–50s.

First, in contrast to the Sinkiang paintings, the pre-Islamic wall paintings from Soviet Middle Asia were laid on loess plasters. These plasters were sometimes lacking in finely cut fibres and were often totally adhered to the raw ground of the building walls. When attempts were made to separate the plaster from the wall even by small pieces, portions broke and were reduced to dust. The colour layer and the ground were unstable, a problem inherent in monumental paintings of the pre-Islamic period from Middle Asia such as the Sinkiang paintings. The surfaces were badly polluted with eroded loess. They required consolidation of the colour layer to the under-layer of plaster before primary cleaning could be carried out, and before the paintings could be removed from the walls. Experience with the preservation of the Sinkiang paintings showed that the materials which had been used previously for consolidation were inadequate. In the Northern climate several problems were seen: spirit varnish caused the paintings to darken over time; and the application of water glues and gypsum resulted in the absorption of water from the air, the formation of salt crystals, and the ageing and peeling of dyes. Moreover the weight of the plastered made it very difficult to store them and especially to transfer them from one store-room to another or to exposition halls. During transfer, large, heavy and fragile plastered plates were frequently damaged at the corners and even cracked completely in half.

Based on the achievements of modern chemistry, Kostrov decided to use synthetic resins and glues in nonaqueous solvents which would not erode the loess ground and glue paintings, such as polyvinyl acetate (PVA). PVA was later replaced by the more stable polybutylacrylate (PBA) dissolved in spirit-benzol, and later this was replaced by the most stable synthetic resin—polybutylmethacrylate (PBMA) dissolved in xylol.

A number of tests confirmed the correctness of Kostrov's choice. At that time PBMA in a xylene base was the best material for the consolidation and removal of the old Middle Asian monumental paintings from the walls and for their transportation to sites for laboratory research work, exhibit preparation, and prolonged storage. Kostrov himself developed and verified the whole restoration procedure using PBMA, including the selection and checking of the necessary instruments and equipment. Without going into detail, let us note that the restorers at the workshop began by applying a mastic of colophony mixed with natural bees-wax, and then applied a zinc-coated iron sheet. With a few technical alterations, the technique of synthetic resin application used for the old Middle Asian wall paintings was also used for clay-giant sculptures, carved wood and other artifacts. Kostrov studied the technique and methodological features of Middle Asian paintings and sculptures in the course of working out his methods of restoration and conservation. At her workshop, I.L. Nogid worked out a method for the removal of salts from paintings on a loess ground and from clay sculptures: the salts were removed from separate fragments of wall-paintings or sculptures by dipping in special baths and by electrodialysis.

The research of Kostrov, E.G. Shejnina and other of his followers provided the basic techniques for the conservation and restoration of samples of monumental paintings on clay plaster, loess, loess-gypsum and partially gypsum sculptures which were excavated by Soviet archaeologists in different places of Middle Asia. Moreover, some archaeologists and restorers in Uzbekistan studied and used the Hermitage techniques. In Tadzhikistan in 1971 a special restoration laboratory headed by L.P. Novikova was formed as part of the Institute of

History. This laboratory was named for Achmad Donish, of the Tadjic Academy of Sciences. In this laboratory, new methods of preservation and restoration were established based on the techniques developed at the Hermitage Museum for the numerous art monuments from archaeological excavations throughout the Republic.

The VNIIR restorers worked on expeditions in Soviet Middle Asia, including Baktria, Sogd, Parthiana, Margiana, Khorezm and Seven River (Siemiretchje). They followed the methods recommended by Kostrov and his school. The VNIIR restorers also applied these methods of conservation and restoration during the joint Soviet-Afghan archaeological expedition as well as during the repeated restoration of paintings and sculptures at the Kabul National Museum. Finally, the methods of Kostrov and his school were used with success during the restoration of the old wall-paintings from Pskov, and the VNIIR restorers also used the Hermitage methods during the restoration of the monumental paintings of Smolensk.

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A bibliography in Russian is available from the authors.



# Working Group 12

Care of Works of Art in Transit

Protection des oeuvres d'art pendant le  
transport





## Abstract

This contribution presents two art-in-transit case studies where surface texture changes on the paintings of E.-L. Kirchner and A. Sisley were successfully detected. The changes were identified using the VASARI system, which allows one to digitally image paintings in high resolution before and after transportation. Appropriate software tools were developed to detect microcracks, deformations, and losses, highlighted as differences between the before and after images. The evaluation principles are given. As a result of this study, a methodology to control art in transit has been developed, and indications have been obtained that the paintings have undergone changes sometime between the acquisition of the digital image(s) before and after transportation.

## Keywords

Art in transit, transportation damages, paintings on canvas, digital imaging, image processing, VASARI system, E.-L. Kirchner, A. Sisley

## Locating Transportation Damages by Digital Imaging: Two Case Studies

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Dedicated to Christian Wolters

## Introduction

Art in transit is a controversial area of conservation, and there are at least as many views and interests as there are professionals involved in the transportation process. Opinions range from not loaning any of the entrusted objects, to a general loaning restraint, and even finally to statements such as "Modern shipping techniques and equipment can now virtually guarantee a safe journey of artworks" (1).

Recent publications have addressed the optimisation of the transport event itself, the method of transportation (including the choice of the route and the type of packing), and the control of the environment in the packing case with special focus on vibrations, temperature and humidity (2). However, little attention has been given to the question: Is there any difference in the condition of the object before and after transportation? We think that this is the key question.

Surprisingly, not many have tackled this question and published results. Early papers by Wennberg and recent contributions by Baribeau *et al* describe attempts to image and compare the condition before and after a distinct event (3-6). Whereas Wennberg studied paintings in a real transportation situation by photography, Baribeau *et al* report an example of a painting that was placed on a vibrating table to simulate transportation stress in an worst case scenario. Their laser scanner allowed an accurate digital representation of the painting's surface. We recently were told that these representations are now superior to those published (7). Wennberg and Baribeau *et al* restricted themselves to pre-selected details of the paintings. In both cases, any comparison of images, e.g., the localisation of surface texture changes, is done by visual inspection.

## Methodology

In a different approach presented here, we use recent information and technology from the field of digital imaging. We aim to represent the painting's surface in full size and with high resolution. The comparison of the images taken before and after transportation ("before" and "after" image) can be done independently from the human observer. Appropriate software tools indicate any change of the surface texture. The results are judged by visual inspection, using the unprocessed "before" and "after" images. If differences between the two images are found, they are noted as either a beginning of a change of the painting's surface texture, or as a damage. We define these damages as transportation damages (8). Surface texture changes and transportation damages not only happen during shipping, but also during in-house handling and moving, such as during hanging, (un)framing, photography, or (un)packing.

Our project at the Doerner-Institut drew benefit from the European research project VASARI (ESPRIT II No. 2649) that allowed us to set up a digital image acquisition and processing system. The system is described elsewhere in more detail (9). It combines an easel, a 3-D repositioning unit, a high resolution CCD camera, and a UNIX-based workstation. The latter controls the repositioning unit and provides the user with a wide range of digital image acquisition and processing tools that are handled with specially designed human-computer interfaces.

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Our methodology to detect surface texture changes using the VASARI system, including the first applications, has been recently outlined in detail (10). In the present paper, two additional case studies are described.

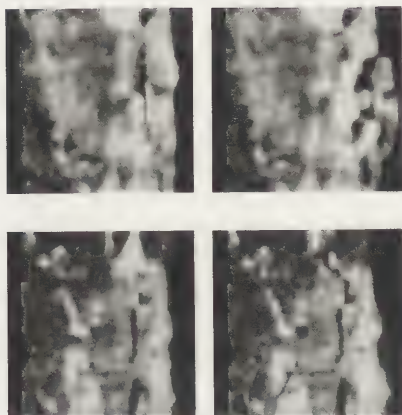
### Case Studies

The two case studies are paintings from our collection that went on loan to different exhibitions. Both passed the thorough, regular condition control procedure by the conservator responsible for the loan arrangements. The paintings were digitally imaged full size with the VASARI system ("before" image). This is done in black and white which was considered sufficient for our purpose. The spatial resolution is about 20 pixels/mm. During acquisition the environmental conditions are carefully controlled. Subsequently, each painting was handled, packed, and shipped as usual. After having returned from exhibition, a second image ("after" image) was taken under the same conditions as the "before" image.

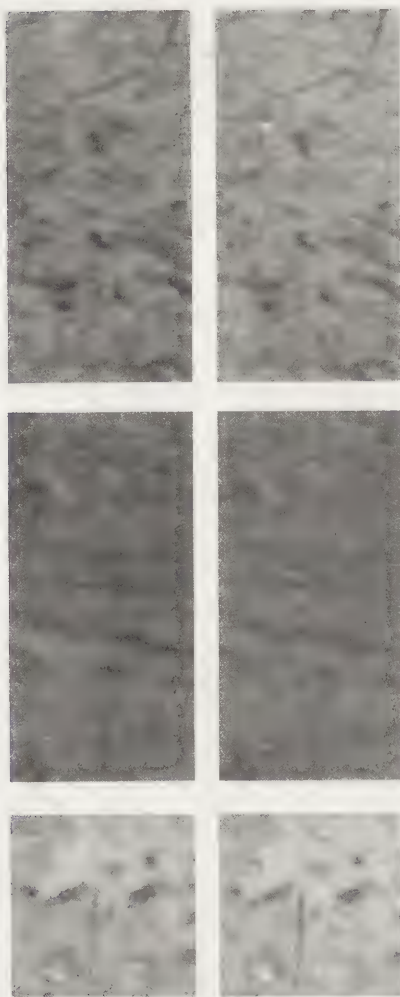
The two paintings were (1) E.-L. Kirchner, *Kartenspieler Knabe*, oil on canvas on stretcher, 69.3 × 62.3 cm (Bayerische Staatsgemaldegammlungen Munchen) and (2) A. Sisley, *La Route de Hampton Court*, oil on canvas on stretcher, 38.8 × 55.4 cm (Bayerische Staatsgemaldegammlungen Munchen). Each had been packed into an insulated case consisting of soft fibre board, polyethylene cushioning, aluminium-laminated polyurethane foam plates, and a plywood case. The Kirchner went by truck, and the Sisley travelled by truck and aircraft.

### Evaluation procedure

- A. Given the resolution, one single image covers an area of only about 10 × 13 cm. Therefore, a set of sub-images had to be taken by displacing the VASARI camera with the repositioning unit. For the Kirchner 5 × 8, and for the Sisley 5 × 4 sub-images (7 MB each) were acquired. The acquisition time for one sub-image is about 3 minutes. The painting is kept strictly static and is not disturbed during image acquisition. The resulting amount of data per acquisition, i.e., 280 MB for the Kirchner and 140 MB for the Sisley, cannot be easily handled. After acquisition, the data is therefore compressed and stored on tape. For subsequent image processing, the data must be read and uncompressed again. During image processing the amount of data can, at times, grow to 1 GB or more. To allow surveying the painting in full format on the monitor, the sub-images are shrunk to a manageable size. The shrunk sub-images are then merged to obtain a full representation of the painting (survey image). This survey image is the base for the protocol image to be introduced later under C.
- B. The next evaluation step is to search for differences between the "before" and "after" images. To do so, the uncompressed sub-images are processed to allow for an easy comparison. This processing includes resampling of the "after" images for later superposition with the "before" images and crack-detection algorithms that have been written for the specific painting. The main intention is not to substitute the human observer, but to indicate where changes of the surface texture may have happened. To enable a fast identification of the changes, regions with no changes are represented black or grey on the monitor, whereas actual changes are highlighted in colour. Finally, the resulting indicator image is used to conduct a thorough comparison of related details in the "before" and "after" sub-images. The Figures 1 and 2 show a set of indicator images juxtaposed with the related details on the "before" and "after" sub-images. To support the user, we are aiming for an automatic computer-generated summary of changes which will range from large to minor changes.
- C. If the set of changes has been clearly identified, their location is given in a protocol image where (coloured) spots or characters are introduced into the survey image. The spots allows one to obtain a quick impression where differences are located. The characters in figure 3 actually relate to the regions on the Kirchner shown in figures 1a and 1b, those in figure 4 to figures 2a-c. Details from the high resolution sub-images also help to visually zoom into the area where differences have been found.
- D. The images A to C—giving the location as well as a close-up of the differ-



1 Kirchner, details of the "before" (left) and "after" (right) images. 1a) deformation and baking of the paint layers, and 1b) prolongation of (micro)cracks.



2 Sisley, details of the "before" (left) and "after" (right) images. 2a) top, 2b) middle, and 2c) bottom, widening and prolongation of cracks.





3 E.-L. Kirchner (for more details about the painting see text), digital protocol image on the base of the survey image with indicated differences (squared spots), as well as the two changes a and b shown in figures 1a and 1b.



4 A. Sisley (for more details about the painting see text), digital protocol image on the base of the survey image with indicated differences (squared spots) and the three changes a, b and c shown in figures 2a, 2b, and 2c.

ences—are used during a discussion of the results while inspecting the actual painting itself. This final evaluation should be done most thoroughly, while bearing in mind that any result of image processing is dependent on the quality of the “before” and “after” images. Moreover, in our experience, the final agreement on a set of changes or transportation damages can only be confirmed while being in front of the painting. In practice, their identification is not always easy and therefore not quite definite even when using a microscope.

### Results

In case of the Kirchner with its brittle and thin paint layers, most of the detected differences are located along the right and the top edges of the painting, whereas nearly no differences are found toward the centre. Because of a slight over-exposure, all the images on the left and lower edge could not be properly processed and evaluated. In these areas, additional differences might be found when applying specially adapted image processing tools. As shown in figures 1a and 1b, flaking, deformations, and a prolongation of cracks on the right edge could be unambiguously proven.

On the other hand, for the Sisley, most differences are located in the centre of the painting, mainly in the sky. Typically, microcracks seem to be widened and/or prolonged whereas deformations or even losses could not be observed. The sensitivity of the procedure can be noticed from a single hair of about 3 mm length on the “before” image, which obviously has been dusted away before the “after” image was taken. This hair appeared as a coloured highlighted difference on the indicator image.

### Conclusions

Compared to previously published work or the common practice of transportation condition control, the procedure proposed here is an obvious improvement. The VASARI approach, although still being a pilot project, allows the detection of transportation damages. Because the approach is not restricted to pre-selected details, an unprejudiced control of the full painting is possible (11). Being largely independent of the human eye, the condition control is more objective. All results can be related to actual changes and can be used to objectively prove surface texture changes and transportation damages. However, the technical development of the procedure is still ongoing.

For both paintings, the changes are basically restricted to micro-cracking or to deformations which may starting points for further damages (raking damages, blisters, and losses). Furthermore, using our approach, different kinds of changes can be detected. In our previous publication, losses along the edges of a painting could be observed which, however, were mainly caused because the painting, for experimental reasons, was shipped in a regular insulated case, but without a protecting frame (10). Nevertheless, even under regular transportation conditions, as for our two case studies, the surface texture of the Kirchner and the Sisley had changed. Thus far, we are not able to trace back these changes to any causes. However, the main purpose of this contribution—address the question if there are differences between the condition of the two paintings before and after transportation—can be answered affirmatively.

### Acknowledgements

The authors would like to thank the European commission (ESPRIT II D. Gonthier DG XIII) for financial and logistic support given to the VASARI project. This case study could not have happened without the collaboration of all the other VASARIs, which is gratefully appreciated. Finally, we would like to thank P. Powell who improved our English captions.

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## Abstract

Using strain gauges, an investigation was made into the dimensional stability of wood in closed cases when the temperature was varied. The study indicates that wood samples sealed in the case without moisture buffering materials exhibited smaller fluctuations in dimension than the wood that was buffered with a material such as Art-Sorb.

## Keywords

Packing cases, hygroscopic materials, moisture sorption, humidity buffering materials, dimensional change, moisture content, temperature, relative humidity

## Measurement of the Dimensional Change of Wood in a Closed Case

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## Introduction

Recent research on packing cases in transit has emphasized that the dimensional stability of hygroscopic materials such as wood, glue, and canvas in the packing case would be achieved by keeping the moisture content of the materials constant as opposed to keeping the relative humidity constant (1, 2).

Packing cases are susceptible to changes in temperature during the course of transport and, as a consequence, the interior temperature is affected. Maintaining constant relative humidity does not create an appropriate environment to maintain constant moisture content in hygroscopic materials. In order to realize a constant moisture content, a simple method has been suggested. Objects should be covered with waterproof materials, such as polyethylene sheeting, to enclose a small amount of air. Then, they should be protected by thermal insulation to prevent rapid changes in temperature.

The purpose of this paper is to verify the approach mentioned above by means of an experiment to measure the dimensional change of wood directly placed in three packing cases with varying environments.

## Measurement of dimensional changes of wood

Three pieces of Japanese cypress (labeled "a," "b," and "c"), weighing 70 g each, were used in the experiments. Measurements of the dimensional variations of the tangential movement of the wood was performed using strain gauges.

Wood sample "a" was packed in a polypropylene case containing 1 liter of air. All edges of the case were sealed with waterproof tape. Wood sample "b" was put in a similar case in which 20 g of Art-Sorb was added as a moisture buffering material. Wood sample "c" was placed directly in the environmental test chamber. The test chamber and the polypropylene case were equipped with thermistors and relative humidity sensors to measure the environment.

The temperature inside the chamber was programmed to change periodically between 40°C and 10°C while the RH was maintained at about 60% RH inside the chamber. Measurement of the temperature, the relative humidity, and the wood's dimensional variations were conducted every 15 minutes.

Each piece of wood was then coated with an acrylic varnish to retard the rate of exchange between the wood and the surrounding air. The coated three pieces of wood were placed in the chamber, and the test procedure described above was repeated. Figures 1, 2, and 3 show the results of the measurements.

It can be seen in Figure 1 that when the temperature rose rapidly, the relative humidity inside the polypropylene case initially decreased. After a short time, the wood began to give off moisture and the relative humidity began to rise. The reverse situation occurred when the temperature dropped. Since 70 g of wood per 1 liter of air exceeds the 1 kg wood per 100 liter of air threshold discussed by Thomson, relative humidity changed in the same direction as

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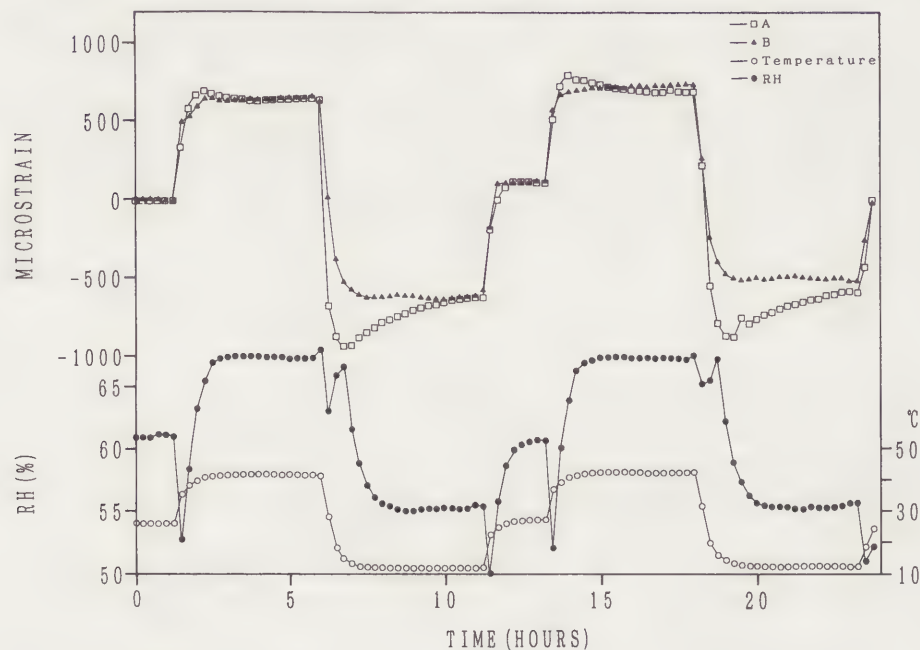


Figure 1. Dimensional variations of Japanese cypress "a" as for the tangential direction packed in a sealed case. The case was placed in an environmental chamber where the relative humidity was kept at nearly 60% RH while the temperature was varied between 40°C and 10°C. Line A represents the dimensional variations of the uncoated samples. Line B represents the dimensional variation after coating the wood with an acrylic resin.

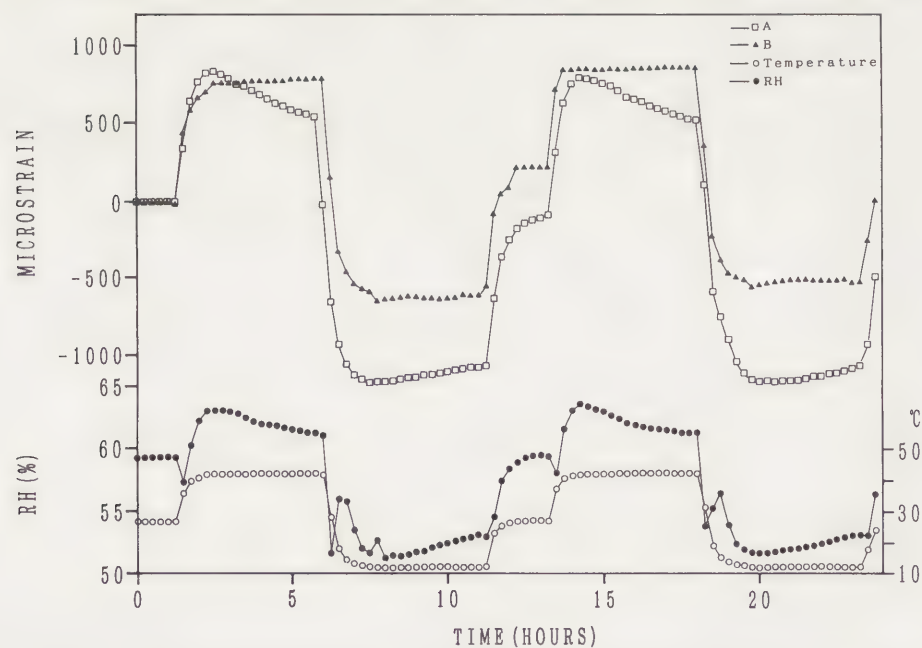


Figure 2. Dimensional variations of wood sample "b" enclosed in a sealed case with Art-Sorb.

temperature (3). The variation in relative humidity was 45% of the variation of temperature in the case containing wood sample "a" and 28% in the case containing wood sample "b" together with Art-Sorb.

### Dimensional changes caused by moisture sorption of wood

Our present concern is confirmation of the relationship between moisture sorption and the dimensional response of wood within a sealed space. It has been shown, however, that temperature changes in the transport environment also have a very significant effect on the dimensional behavior of the wood (4). It can be concluded, therefore, that the dimensional behavior of the samples before coating with acrylic varnish results from the combined effects of moisture sorption and temperature variations (See line A in figs. 1-3). After coating with varnish, we obtain the dimensional response caused primarily by temperature changes (See line B in figs. 1-3). The dimensional change caused by the moisture

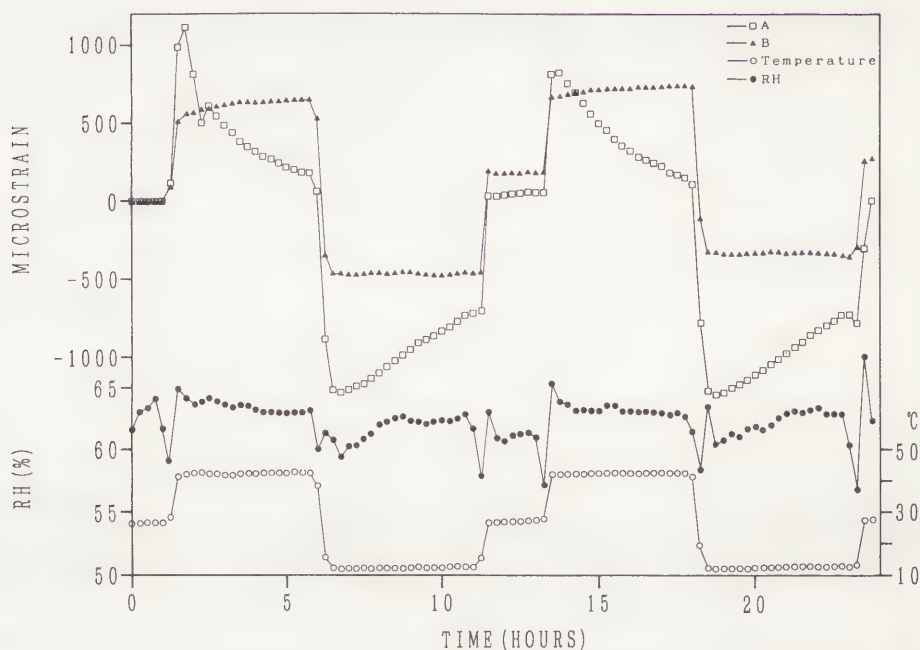


Figure 3. Dimensional variations of wood sample "c" placed directly in the environmental chamber.

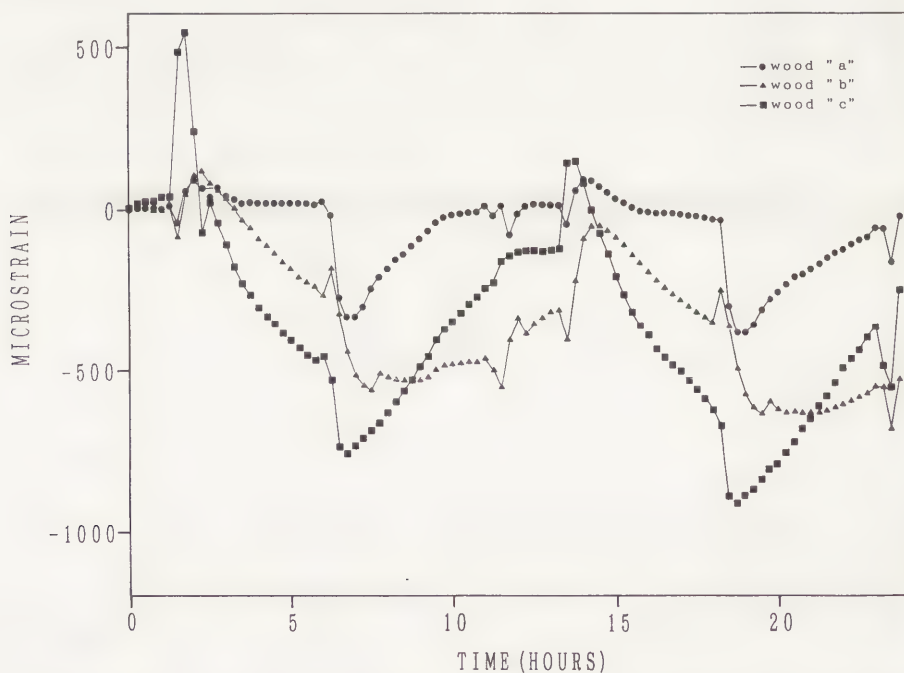


Figure 4. Calculated values obtained by subtracting the dimensional variations of line B from line A for the three wood samples.

sorption of the wood is obtained by subtracting the values presented in line B from the values presented in line A.

Figure 4 shows the calculated dimensional variations of the wood pieces in the different test conditions. The smallest change in the moisture content of the wood is found with wood sample "a." This is true because there was little air for the wood to exchange moisture.

When a moisture buffering material such as Art-Sorb is added in the case, it is apt to absorb and desorb the moisture from the wood because of its high sorption capacity. Although the total amount of moisture does not change in the case, Art-Sorb controls the moisture content of the wood and air. It can be seen that wood sample "b" moved significantly when the temperature changed.

Because the total amount of moisture is constant inside the cases, the moisture lost by the wood is gained or lost by the air and Art-Sorb. When the wood gets



hotter as the temperature of air rises, it gives up the moisture and begins to shrink. But at the same time, the heat makes it swell because of thermal expansion. When the wood gets colder, it shrinks because of the temperature change but swells because of the absorption of moisture.

Wood sample "c" exhibits the largest dimensional variation due to moisture because the relative humidity in the chamber was maintained as constant as possible during the changes. This meant that there was always a constant interchange of moisture between the wood and the air.

An uncertain point exists concerning the behavior of the relative humidity within the case. When the temperature decreased, the relative humidity initially decreased, and then the relative humidity started to increase rapidly. After reaching the maximum, the relative humidity started to decrease along with the temperature as before. This result was also observed in another experiment using a case containing wood, for which we do not have a clear explanation.

### Conclusion

This research examined the dimensional behavior of wood when it was enclosed with a small amount of air and subjected to a temperature variation between 40°C and 10°C. The measurements revealed that wood enclosed with little air and without any moisture buffering materials is more dimensionally stable than wood enclosed with a buffering material such as Art-Sorb.

It is confirmed that adding a moisture buffering material to stabilize the relative humidity actually lowers the dimensional stability of wood if the buffering material has a higher sorption capacity than wood. It can also be concluded that the best dimensional stability will be attained by reducing the temperature variations by means of increasing thermal insulation and controlling the transit environment.

All of these facts support the legitimacy of the packing method that is designed to keep the moisture content of objects at a constant level, not to create constant relative humidity inside the case.

### Materials

Art-Sorb: silicon dioxide, Fuji-Division Chemical LTD., 2-1846 Kozojichyo, Kasugai-shi, Aichi Pref. 487, Japan.

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# Working Group 13

Natural History Collections

Collections d'histoire naturelle





## Abstract

On February 16, 1990, a fire burned in an unfinished gallery at the Saskatchewan Museum of Natural History in Regina, Saskatchewan. Soot was deposited on all surfaces of the building and its contents. Museum conservators gained a deeper understanding of fire prevention and suppression and were alerted to the importance of smoke suppression and containment during a "modern" fire involving fire-retardant materials. The disaster recovery process involved not only museum staff, but also a multitude of external inspectors, managers, and commercial firms. Within the context of the fire in Regina, conservators investigated the role of external agencies in the vital decisions and procedures following a museum fire.

## Keywords

Fire, soot, smoke, natural history, disaster planning

## Fire Recovery at the Saskatchewan Museum of Natural History: Part I, Description of Events and Analysis of Recovery

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## Introduction

Fires may initiate within a museum or may spread from a neighbouring building. The risk of fire should not be underestimated; there were at least 27 museum fires in Canada between 1970 and 1990 (1).

## The fire

The Saskatchewan Museum of Natural History (S.M.N.H.) is divided into two buildings. The main museum building houses the exhibits, mounted specimen storage, and some offices. The curatorial offices, workshops, and some remaining storage areas are located in a building across the street. The galleries, designed in the 1950s, were in the midst of a long process of renovation and reconstruction at the time of the fire.

On the evening of February 16th, 1990, an insulation company was brought into the new First Nations (native Indian) gallery to inject two-part polyurethane foam insulation behind a hollow replica rock wall. A museum technician, who had been retained to watch over the contractors, turned to the local news later that evening to learn that firefighters were at the museum unsuccessfully trying to locate the source of a fire. The technician, suspecting that he knew the location of the fire, rushed to the scene and led firefighters through the dense, black smoke to the rock wall. The fire was extinguished within minutes.

The unofficial cause of the fire was self-ignition of the foam when released heat was trapped between the resin/fibreglass rock wall and the fire-separation gallery wall. The foam, and eventually the materials surrounding it, burned until an ionization smoke detector in the central return duct registered the presence of smoke. This triggered the vigilant alarm system, which alerted the fire station. Firefighters arrived at the building only two minutes later, but saw no evidence of fire. A minute later, thick billows of smoke appeared in the windowed lobby and firefighters broke into the smoke-filled lobby. This incredibly rapid smoke build-up, typical of a modern fire, combined with other factors to prevent the crew from finding the fire until almost an hour later (see the Fire Department section in this paper).

The modern construction materials in the gallery—fire-separation walls, steel studs, and fire-retardant gyprock—prevented ignition of the wood structure of the original museum building. However, the smoke generated by the fire followed the predominant air current further into the First Nations Gallery. As smoke accumulated, it travelled through ducts, left open during construction, into the Life Sciences Gallery located on the upper floor. It then travelled down the aisles and stairs and by air current through the ductwork, to the rest of the building. The rapid and intricate spread of this thick, black, sticky smoke proved to be the greatest tragedy of all.

While the gallery was under construction, some basic precautions had been neglected. Smoke detectors at the site were capped in order to avoid being

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clogged by dust produced during renovations. Although this is standard practice on construction sites, caps should have been removed at the end of each work day. A fire-watch consisting of a patrol of the renovation site at the end of the day and a few hours after site closing should also have been implemented. Generally speaking, the need for a fire watch can be incorporated into a contractor's agreement (2,3).

Fire alarm and suppression systems had been designed to code, which was insufficient protection for collections. The building lacked a fully zoned fire alarm system and sprinklers. Fire alarm and security systems in the building were also compromised during renovation. There was no indication as to the location of the fire because the annunciation panel, which records the location of first alarm, was in a place unknown or not visible to the firefighters. Firefighters discovered that their entrance into the building and their movement within the building was barred by doors closed tight with magnetic locks. A new security system that was to incorporate automatic opening of doors in event of a verified fire had not been completely installed when the fire occurred.

There were some positive elements that mitigated the disastrous effects of the fire: 1) fire-retardant material used in the construction of the gallery slowed the spread of flames; 2) firefighters were very sensitive to the nature of the building's contents; 3) there were no objects in the fire-ravaged First Nations Gallery (fitting of objects in cases was done with replicas to minimize artifact handling); and 4) the vigilant alarm system automatically alerted the fire department and saved the museum from a much greater loss.

### The building

After the fire, the building had a bitter smoke smell. It was entirely blackened with a thick blanket of soot; no surface could be touched, walked on or sat upon without the transfer of the black powder. Mechanical and electrical systems were shut down.

The First Nations Gallery, which had been a series of white, freshly plastered curving walls and empty cases, was covered with a thick, matte, black soot layer. The walls, white to a certain point, were black to the ceiling where the soot-filled air had accumulated (see fig. 1). Nearest the burn site, the soot on the walls formed web-like filaments up to an inch long and farther from the burn site, the soot covered surfaces with a fine powdery mat.



Figure 1. The First Nations Gallery, under construction, is blackened with soot.

At the burn site, a few portions of the blackened replica rock wall clung to the remains of gallery walls. Metal ducts and tools and equipment left from the



day's work were deformed and everything in the area had been partially incinerated by the intense heat. The fire separation wall and fire door (closed at the end of each day) at the burn site had adequately prevented penetration of the fire to the neighbouring Earth Sciences gallery, but soot had travelled through ducts, settling on a thick layer on all surfaces; above the dropped ceilings, it infiltrated sealed cases through the small holes used for the installation of lighting. Some surfaces were more sooty than others, for example, plastics seemed to attract the soot (see fig. 2). Soot was also deposited according to air current, gathering at the end of curved walls where the air and soot had been funnelled.

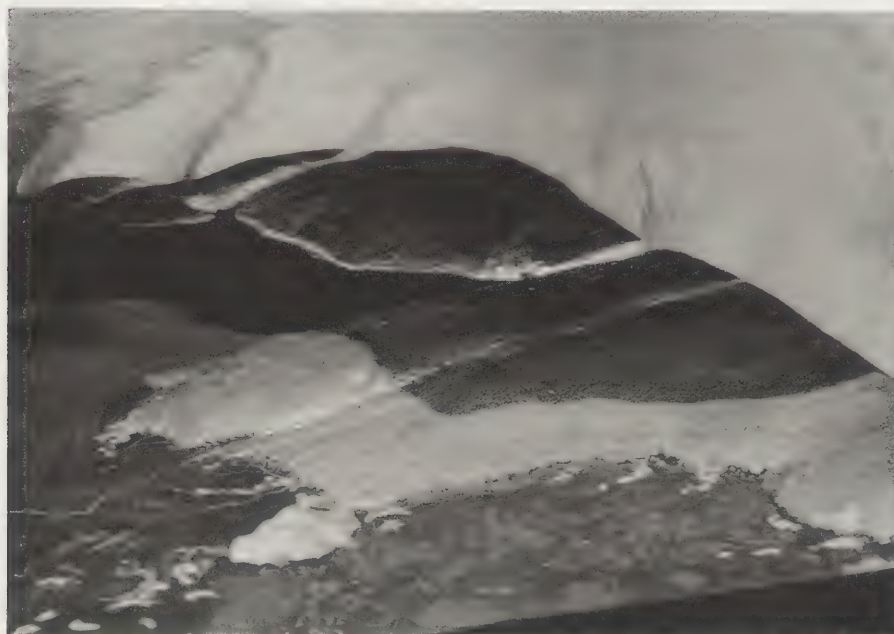


Figure 2. A white glacier exhibit (acrylic paint and varnish on sculpted styrofoam) vacuumed at the front, fully cleaned at the back, and untouched in the middle section.

The Life Sciences galleries located on the second floor contained birds and animals on natural foregrounds in dioramas. The diorama shells (acrylic paint on plastered forms or commercial tempera on primed canvas marouflaged to gyprock) were pushed tight, but not sealed to glass fronts. The fine soot penetrated this small air space, depositing in such an even fashion that the full extent of damage was not immediately apparent.

Bird storage was located in the basement far from the burn site in closed units. Soot carried through the ductwork infiltrated cabinets and drawers, and settled in a thin layer on the approximately 1500 mounted specimens.

### External agencies

The severity of damage to building, grounds, furnishings and collections and the complexity of recovery will force a fire-ravaged museum into a working partnership with several external agencies and persons. At the S.M.N.H., those who descended upon the damaged building—the insurance company representative or adjuster, subcontractors, cleaners, and property management—had well established roles and procedures in post-fire recovery. Museum staff, lacking a disaster contingency plan, scrambled to make rapid decisions and vocalize priorities.

The authors are convinced that a recognition of all external agencies that will become involved in a post-fire recovery and communication with such agencies to clarify their roles should be an integral part of a fire contingency plan. Within the context of this fire, S.M.M.H. conservators investigated this aspect, and a general description of the findings is described below.

### Owners

A museum may not be the sole owner of the museum and its collections. Governments, boards of directors, museum "friends," organizations, property

and grounds management corporations, or private individuals may wield ultimate authority in certain areas of disaster recovery, and this will certainly affect rapidity and priority of the recovery of collections. All such "owners" should be included in and authorize a disaster plan.

In most of the reports on museum fires, it is noted that individuals and groups who have little day-to-day involvement may have an important say when it comes to major events such as disasters. Conversely, a conservation staff that has gained a measure of respect in everyday matters may be ignored after a fire because they are perceived to lack experience and expertise in this area.

At the S.M.N.H., the collection was owned by the museum (which was ultimately owned by the governing institution, the provincial government). The building was owned by a provincial government property management corporation, the grounds by a municipal authority, and the gift shop by the museum "friends." Each "owner" had its own project manager and its own vested interest and priorities. For example, the priorities of the building's owners were such that they feared soiled objects would recontaminate their cleaned building. The museum did not have authority over personnel; temporary technical staff could only be hired by the government personnel department, which led to months of delay hiring staff to aid in recovery, as well as inadequate screening of applicants.

In the matter of authority within a museum during disaster situations, the authors believe that while certain problems may be avoided by involving conservators in all decision-making that affects the collections, the most effective means of ensuring collection safety is to educate upper management in recovery priorities. These individuals are in a position to cut through red tape at a time when speed and efficiency are of paramount importance. It is easier to instill an understanding of conservation concerns before a disaster strikes than to try to change an entrenched hierarchy in the midst of an emergency.

### **Insurance**

The insurance adjuster is hired by the insurance underwriters to interpret and carry out the intent of the insurance contract. The insurance agent may be contacted at the disaster planning stage in order to discover what the coverage is and how the extent of coverage impacts on the recovery work for the building, its furnishings, the grounds, and the collection. The insurance adjuster will be a vocal part of the decision-making team and should be chosen during the disaster planning process (termed an "adjuster of record") through the insurance agent. The adjuster should be made sensitive to the needs of a museum and to all aspects of the contingency plan, including the specialists within and outside the institution who may have expertise in disaster recovery, appraisal, and conservation.

At the S.M.N.H., collections were "self-insured" by the government, which meant that costs associated with collection cleanup had to be managed almost entirely out of the annual budgets of the museum. The building was insured through the property management corporation.

### **Construction manager and subcontractors**

The especially destructive nature of this disaster meant that not just the collection, but the building itself had to be restored and, indeed, this may be the first priority for many of the decision-makers. If part of a collection cannot be physically moved from the building before it is fully cleaned and refurbished, the methods and materials involved in building restoration will impact significantly on conservation of collections. As a member of the disaster planning team, a conservator can work to balance the needs of the collections and of the building.

To ensure the smooth process of large-scale building refurbishment and reconstruction, an insurance adjuster may elect to hire a project management company, normally connected to a construction firm. The construction manager ensures better cost control, provides constant supervision, completes general construction



tasks that fall between the mandates of subcontractors, and serves as a liaison between subcontractors, owners, and the insurance adjuster. Local firms should be researched as part of disaster planning. A chief organizer of all the trades who is informed of the museum's recovery priorities and of special needs can regulate working procedures accordingly. The museum and other owners (e.g., the building owners and gift shop owners) may write their own specifications for the construction company and subcontractors prior to a disaster. The general specifications may include such points as the disclosure of material formulations and techniques, handling and care instructions, and even design requirements and paint colour formulations.

An up-to-date list of post-fire building restoration companies should be an appendix to the disaster plan. These specialized cleaners handle all facets of building cleanup, including walls, ceilings and ductwork, decorative finishes such as carpets, and furnishings. Companies may be researched to determine their capabilities, including types of equipment available, experience, and degree of understanding of the needs of the museum. It is to the institution's advantage to meet with a pre-selected company to identify roles and clarify methods and materials involved.

In Regina, the conservation and salvage teams arrived on the scene completely unaware of each other's existence until that moment. The construction project manager tried, sometimes successfully, to coordinate the needs of subcontractors and conservators. Some problems were encountered, such as the shifting by subcontractors of carefully placed protective polyethylene sheeting, and the fact that conservators were unaware that HVAC fans were left running to clear the air, causing airborne soot to settle onto cleaned collections.

### **Fire department**

The local fire station must be contacted for assistance with a fire disaster plan. In Regina, the fire department will produce a "preplan" which is used to aid firefighters at the scene. Preplans include, among other things, a site plan and a layout of each floor with locations of interest, for example, flammable materials storage, water cabinets, etc.

Museum representatives can make special additions to the preplan to ensure maximum protection for collections in the event of a fire. Such points include designating secondary search rooms that will only be entered if the fire cannot be found elsewhere; this will protect particularly sensitive collections from the unnecessary influx of smoke.

Preplans, if locally available, should be updated every time areas in the museum are altered, for instance, when changing the design of exhibit rooms. A copy of the preplan should be kept at the museum; the technical details found in the preplan could be useful as appendices to the museum disaster plan.

Arrangements should be made to tour all the shifts of firefighters from all responding stations through the museum; in this way, those who will actually be searching the building will be better prepared. An open house for the firefighters could be held whenever major exhibits change. This is a proven method that is not used enough and that should also be extended to the police department. At the same time, the museum should present the fire department with its emergency evacuation plans and details of its fire prevention activities. These may serve as the basis for an improved prevention plan.

The fire department in Regina noted the factors that combined to make fire-fighting difficult and hampered discovery of the fire's location:

- a) the winding design of the new galleries
- b) fire hoses that did not reach to the end of the galleries
- c) the recent renovation whose design was unfamiliar to the firefighters
- d) security doors that remained locked throughout the fire search
- e) keyed doors inside the building that locked behind the firefighters
- f) the thickness of smoke, which forced a search on hands and knees
- g) the heavy smoke and lack of flames that prevented easy sighting of the fire

### Smoke containment

The National Building Code of Canada is designed primarily for life safety, with property protection being incorporated insofar as it applies to preventing the spread of a fire to other buildings. Building contents are viewed only as possible hazards, and specific provisions are not made for safeguarding them. An architect who is not aware of the special needs of museums may, therefore, design according to a code that falls short of protecting collections. The problem of smoke damage is a prime example.

The S.M.N.H. fire involved a typical two-part, fire retardant foam-in-place insulation found in many buildings. Depending upon the type of materials and flame-retardant systems used in building construction, smoke evolves in varying quantities. The chemistry of fire-retardants is complex, but the literature indicates that, in the future, smoke-suppressant properties will play an increasing role in the choice of retardant systems for polymeric materials (4).

Nevertheless, the problem of heavy soot generation by plastics in modern buildings indicates that museums must consider not only fire containment, but also smoke containment. Smoke detection in modern buildings is best effected by ionization detectors, which spot the products of combustion before soot is generated. Smoke generation can then be controlled naturally by suppression with sprinklers. Paul Baril provides a convincing argument for the installation of sprinklers (5).

A great deal of smoke will be generated in a modern fire, however, before there is enough heat to set off the sprinklers. The quantity of air moved through HVAC systems in museums can slow the build-up of heat considerably. This provides a strong argument for smoke compartmentalization in the fire zone. Normally, the fans in the HVAC system are connected to the smoke alarm and will shut down automatically once this is activated. This basic response would have prevented a certain amount of smoke damage at the S.M.N.H.

Currently, there are at least two options for advanced smoke containment. The first is a system now implemented in hospitals. Dampers that close in response to smoke are installed in ducts and serve to compartmentalize smoke while the exhaust from the fire zone is directed out of the building. The drawback is the high cost of the system. Some museums have a second option. Direct digital control systems controlling the museum environment are easily adapted for smoke containment. Air supply to the fire zone can be decreased and the exhaust, which contains the soot and smoke, can be moved from the room directly to the outside. At the same time, the system can supply air to surrounding rooms to generate a positive pressure and to prevent air movement from the fire zone into the unaffected rooms.

Experience and research have shown that in the "modern" museum room that is fitted with fire-retardant materials and equipped with fire suppression systems, the possibility of smoke damage to surrounding areas may be greater than the possibility of damage from flames. In a museum, even a small amount of soot can cause near destruction of certain collections. Research continues on the effect of a smoke control system on heat detection and sprinkler initiation (6).

### Conclusion

Severity of the fire in Regina was increased by compromised fire detection and security systems during exhibit renovation and by factors that prevented fire-fighters from locating the fire. Fire-retardant materials and modern construction prevented severe structural damage to the building. However, the blanket of black soot deposited by the slow-burning "modern" fire could have been prevented with the use of sprinklers and smoke containment. External agencies and persons that became involved in fire recovery had self-defined authority, roles, and responsibilities; conservators investigated this aspect of fire recovery and concluded that if an investigation of this type was conducted at the disaster-planning stage, other museums would rise more swiftly from the ashes of a museum fire.



### Acknowledgements

Gratitude is expressed to Museum Director Ron Borden for his willingness to disseminate this information and to those persons from external agencies who shared information regarding their participation in fire recovery.

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6. Interview conducted by F. Graham with George Tamura, Senior Research Officer, National Fire Laboratory, National Research Council of Canada, September 9, 1991.

### Abstract

A diorama fire at the Saskatchewan Museum of Natural History burned for over an hour, depositing soot throughout the building and its contents. Cleanup of collection and displays was carried out within the building while it was being cleaned and refurbished. After months of cleaning, a progressive cleaning technique was found effective in treating the problems specific to soot removal. To clean soot-covered feathers, a vacuum wand nozzle was designed. Testing was undertaken for vacuum, dry, and wet cleaning of soot from delicate feather- and fur-bearing mounts.

### Keywords

Natural history specimens, soot removal, disaster recovery, fire, fur, feathers, cleaning techniques, cleaning materials, vacuum nozzle

## Fire Recovery at the Saskatchewan Museum of Natural History: Part II, Post-Disaster Cleanup and Soot Removal

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### Introduction

The fire at the Saskatchewan Museum of Natural History happened February 16, 1990. For a description of the initial stages of conservation responses to this disaster, see S. Spafford and F. Graham, "Fire Recovery at the Saskatchewan Museum of Natural History: Part I, Description of Events and Analysis of Recovery," in this volume.

### Building cleaning, restoration, and refurbishment

Museums cannot always move all collections off-site following a partial or full-scale fire. Even if objects are removed from a building, strong cleaners and sealants remain in the air following application, so products and techniques used by building cleaners and other subcontractors should be detailed and approved at point of bid.

Post-fire cleaning personnel follow a well-defined procedure in the affected building, using cleaning products designed specifically for fire cleanup. The extent of the required soot removal is astonishing, for example, from above ceilings and inside walls and ventilation ducts. Three passes of progressively deep cleaning were undertaken by the building cleaners that serviced the museum. The first stage consisted of removing the nonrecoverable building features and loose soot from all surfaces. Then, deep cleaning was performed with products specific to the commercial cleaning trade. Any porous or hard-to-reach surfaces were sprayed with a thick alcohol-based oil paint. A final pass consisted of cleaning and polishing, as well as deodorization with fragrances.

### Soot and its removal

Soot represents the liquid and solid fragments of pyrolysis, an oily, tarry matrix containing hundreds of compounds combined with carbon. Soot particles are tiny (about 7 microns), but the sticky oils cause it to form loose agglomerations of various sizes.

Samples of soot from the interior surfaces of the museum were analyzed by the Canadian Conservation Institute (CCI Analytical Report No. ARS 2861). The composition represented pyrolysed products of polyester and polyurethane that had burned and mixed with carbon. Soot taken from various places in the museum had identical composition, but had formed different-sized agglomerations. The soot was acidic (pH 4–4.5). The particles were wetted easily and dispersed well in organic solvents, but settled quickly with an extraction of a brown oily residue. Water did not wet the soot and extracted nothing.

Museum conservators conducted cleaning tests during the week following the fire. Hundreds of surfaces—from fossils to diorama paintings on canvas—were tested with vacuums, cleaning tools, and dry and wet cleaners. A chart documented test results and the cleaning time estimates for each area.

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Similar surfaces responded differently to the same cleaner or cleaning technique. Response to cleaning depended upon size of soot agglomerations, "setting" of soot into warm surfaces near the fire, thickness of the soot layer (in turn often dependant upon distance from the fire and the angle of the object surface), attraction of soot to a particular surface, and the time soot was allowed to rest on a surface prior to cleaning. Soot became more difficult to remove as time went on, especially from textured and porous surfaces.

Soot removal differs greatly from the removal of dirt and other accretions, as the soot agglomerations are easily broken into minute particles of carbon which quickly "pigment" or become a part of even the most smooth surfaces. It is the first stages of soot disruption that will determine the ultimate completeness of soot removal. For example, conservators found that if a soot-covered arborite gallery text panel was touched, the ingrained dark fingerprints would remain after cleaning. Direct vigorous wet cleaning of the panel resulted in a grey wash of ingrained dirt, whereas vacuuming followed by wet cleaning of the same surface produced a clean result. It became obvious through trials that the tiny carbon/oil particles of soot must be lifted with little disruption of agglomerations, minimal dispersal of particles, and no extraction of oily compounds (i.e., no attempt to solubilize). An indisputable necessity in the thorough removal of minute soot particles is a progressive cleaning technique using direct vacuuming (this stage, if properly carried out, removes almost all of the soot), dry methods that lift more particles from the surface, and, lastly, wet methods if appropriate.

### **Cleanup of collection and noncollection material**

The museum (management) cleanup committee, insurance adjuster, and property manager made a decision common to post-disaster recoveries: quick cleanup for rapid public access. This meant that some noncollection materials received a higher priority than accessioned collections.

Because it was not practicable to move delicate collections, cases, and dioramas off-site, most cleaning of displays and collections was carried out by conservators within the museum at the same time that the building was being refurbished. Other objects, such as educational materials, were removed to a warehouse for storage and cleaning. Nonrecoverable displays and collections, such as burnt material and diorama foregrounds, were removed by volunteers for disposal.

Organization was paramount, since cleaning involved two conservators, five technical staff, and several volunteers who worked in many locations throughout the museum and the warehouse in concert with building cleaners and subcontractors. Charts with recorded cleaning test results were stored in a master binder, and short written procedures for particular objects or displays were posted to aid technicians and volunteers. Volunteers logged their hours and duties on a sign-in sheet in the lobby. A detailed portable chart noting what objects or areas had been cleaned or partially cleaned at the end of each day was a useful aid in the organization of tasks, since projects often had to be abandoned in progress to make way for commercial cleaners or a subcontractor, and then continued some days later.

Soot cleanup gear consisted of white disposable coveralls and a hat, a fume-filtering safety mask (in the first days of cleanup), a particle mask, and gloves. Cleaning kits at the museum and warehouse consisted of latex and white gloves, several vacuums, cleaning tools and materials (described below), and some household cleaners, small and large pails, polyethylene bottles, solvent dispensers and spray bottles containing wet cleaners, sponges cut to small squares, Webril, and swabs.

One room was set aside within the museum to store cleaning kits and gear, and another to store and clean dismantled displays, objects, and specimens. Objects had to be moved en masse on a few occasions to accommodate a cleaning pass or a subcontractor. At the end of each day, and as each area was cleaned, the dioramas and displays were wrapped in polyethylene to prevent contamination of the cleaned surfaces by airborne soot and construction products.





Figure 1: Vacuum cleaning of the acrylic-painted surface of an eagle diorama shell.

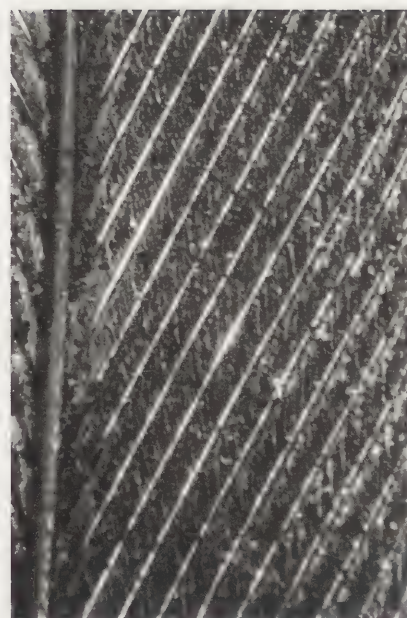


Figure 2: Photomicrograph of soot-covered feather (Canada Jay) before cleaning.

The peculiarities of soot necessitated outlining new rules of handling to aid soot removal and lessen the possibility of particle ingraining. A sooty surface could not be disturbed or touched before application of direct suction to remove soot agglomerations. Vacuuming was done before an object was moved, and objects could not be stacked or wrapped without pre-vacuuming.

Although tested conservation cleaning materials were almost always used, techniques were tailored to the object. For example, a rare dinosaur cast (acrylic media on fibreglass/resin) was cleaned with a vacuum and Groom/stick, and then 2% Orvus on small sponges or Webril. Alternatively, plastic plants from an underwater diorama were swished in garbage pails full of Orvus, rinsed, and left to air dry. Books in a resource library were cleaned by vacuuming *in situ* and by hand, followed by grasping of the text block for further cleaning with Chemical Sponges and art gum erasers and wiping of the cover and spine with Webril. By contrast, paper objects used in education programs were rolled through a paint tray half-filled with Scum-X eraser powder.

### Cleaning techniques and materials

Detailed documentation was kept of vacuuming, dry cleaning, and wet cleaning methods for soot removal from various surfaces.

Vacuuming, the first step in all soot removal, lifted soot with no breakup of agglomerations and involved minimal pressure upon and ingraining of soot. A crevice tool was used directly on a surface in a suction-and-lift technique or elevated very slightly above the surface with a finger under one end of the tool (see fig. 1). Conventional protective techniques (placing a screen over the surface or brushing into a vacuum), caused ingraining of soot which could not subsequently be removed.

Dry cleaning materials and techniques included the use of Groom/sticks, eraser powder, Chemical Sponges, and other materials. Groom/sticks would attract and hold soot from any surface, especially surfaces that could not be wet-cleaned or rubbed, porous materials such as concretions, textured surfaces, and tiny recesses. The textured large crumbs of Scum-X eraser powder effectively lifted and held soot from many surfaces including paper, books, smooth minerals, and hides. Chemical Sponges, designed for commercial building cleanup, were indispensable (1). Rubbed across canvas diorama backdrops, wall paintings, book covers, and smooth stone, rubber crumbs captured and rolled away the soot. Webril, a disposable soft wipe, was used in a gentle lifting motion on smooth and delicate surfaces. Soft goat hair (*hake*) brushes were the best brushes for lifting and holding soot, but were never used in a broad brushing motion. Art gum erasers, kneaded erasers, and tac cloths received some use.

Wet cleaning was carried out where appropriate, often preceded by vacuuming and dry cleaning. Although commonly recommended for soot removal, the oily solvents such as varsol and stoddard received no use, since cleaning tests revealed that they extracted oily components, dispersed small particles, and tended to push rather than lift soot. For wet cleaning, the following aqueous solutions were the most useful: 2% Orvus (effective in almost all circumstances), 2 and 4% ammonia (the apparent cutting action lent itself to cleaning of diorama backdrops of varnished acrylic on canvas and wall-paintings), 2% Aerosol OT, and 3% sodium perborate. Ethanol or an ethanol/water solution was used on shells, stone, and other surfaces where other wet cleaners would have been unsuitable. Solutions were applied on barely dampened swabs, pads of Webril, pieces of sponge, in pails, or spray-applied depending on the surface being cleaned.

### Removal of heavy soot from bird mounts

Birds displayed in dioramas on the upper floor animal gallery were covered with a heavy soot layer. Visible under an operating microscope (See fig. 2), the intricate structure of the feathers had trapped soot on the surface, between barbules of the feather and, in some cases, below the surface and onto feathers below. It



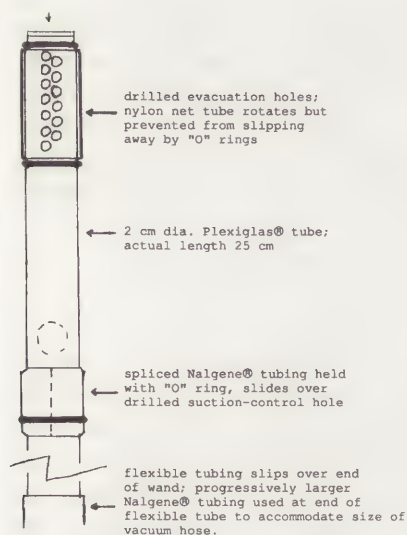


Figure 3: Vacuum wand for soot removal from feathers, front view.

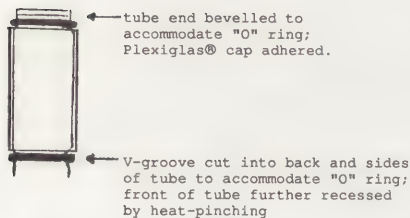


Figure 4: Vacuum wand for soot removal from feathers, side view.

was obvious that any cleaning method that broke soot agglomerations would drive soot deep into the feather mat.

Months of previous experience with soot removal pointed to vacuum suction as the best way to lift soot. A dental evacuator, reported as useful for feather cleaning was too expensive, so experiments were conducted with the museum's high-efficiency particulate air vacuum to develop an attachment with a small and versatile shape, adjustable suction, and adequate protection for feathers with minimal breakup of soot (2).

After several prototypes were constructed, a plexiglas wand vacuum nozzle was developed (See figs. 3, 4). Two rows of extraction holes are drilled into a side of the wand near the tip to allow free movement over the curved parts of a bird of any size. A nylon, butterfly net fabric welded with a hot tip into a tube shape freely rotates over the extraction holes, and a large suction control hole is located at the base of the wand. The wand performed exceptionally well, removing about 85% of the soot from feathers with no disruption to structural condition of the feather as viewed through an operating microscope (See fig. 5). Residual soot was revealed when an overlapping feather was pulled away to expose a protected feather beneath (this shadow was not entirely removed by any cleaners subsequently tested).

Based on methods noted in the literature and personal experience with soot removal, tests were performed with dry and wet cleaners (4, 5). All tests followed use of the vacuum wand and were carried out on feathers removed from the tail of a Canada Jay and on test patches on the back of a mounted pelican. Analysis before and after cleaning was compared to a control that had been vacuumed only, assessed visually under the operating microscope, and recorded on photomicrographs.

The following dry cleaning materials were tested by wiping them over the feather surface: tac cloth, Groom/stick, and Webril wound in 1" wide strips on a long wood applicator stick. Groom/stick and Webril removed about 25% of the remaining soot.

The wet cleaners tested were as follows: Orvus 2% in distilled water/rinse, 1% Orvus in 5% ethanol/rinse, ethanol, trichloroethylene, 1:1 ethanol/trichloroethylene, 1% Vulpex in trichloroethylene/rinse, and 2% ammonia/rinse. Webril pads, barely dampened with cleaners, were applied for 60 strokes along the direction of feather growth. Where a rinse was required, 30 strokes of cleaner was followed by 30 strokes of primary solvent. Wet sites were dried with a stream of cool air.

All water-based solutions yielded approximately 30% removal, leaving a slightly grey appearance, excessive tide lines, and moderate to severe disarticulation and matting of feather barbs. The ammonia solution yellowed feathers. Ethanol removed approximately 50% of the remaining soot, but left no colouration on the swab, indicating that the soot was pulled towards the evaporating edges (tide lines such as this can be minimized through careful technique). The most effective cleaning solution appeared to be 1% Vulpex in trichloroethylene at about 60% removal with little effect on feather structure (See fig. 6, and refer to fig. 2 for the same feather before cleaning). The proven ability of this solvent to remove natural constituents from the feathers and skin is an added consideration (6).

Cleaning methods were chosen accordingly. Dry methods (Groom/stick and Webril) and the wet cleaners (ethanol and 1% Vulpex in trichloroethylene/rinse) were used, alone and in combination, but always after the object was vacuumed with the wand. Cleaning materials were chosen depending on the particular type of feathers being cleaned and degree of soot coverage.

### Removal of light soot from bird mounts

The bird mount collection of 1500 specimens, stored in closed cabinets in rooms far from the fire, had only a dusting of soot. The birds were cleaned using a variety of tools, though the size of the project precluded use of the vacuum

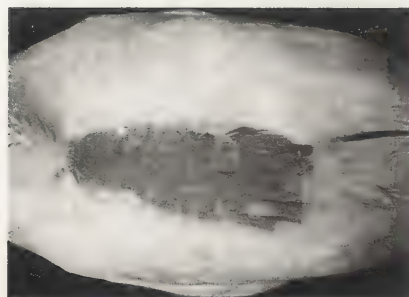


Figure 5: Back of Snow Goose during vacuuming. The dark patch represents the area that has not yet been vacuumed.





Figure 6: Photomicrograph of feather (Canada Jay) after cleaning with vacuum wand and 1% Vulpex in trichloroethylene.

wand. Wood bases were cleaned with a *hake* brush, Chemical Sponge, and Groom/stick. An owl wing was used with a whisking motion in the air to blow loose particles free from feathers, and used then for gentle brushing. Webril in 1" wide strips was rolled several layers thick onto a wood stick and brushed gently over the feathers. Soiled Webril was removed one layer at a time. Tweezers and dental tools were used for some feather realignment. The eyes, feet, and legs of the birds were cleaned with Groom/stick, ethanol, 2% Orvus, or distilled water as appropriate.

### Removal of heavy soot from fur-bearing mounts

Removal of heavy soot from mammals stored and exhibited in the soot-filled upper galleries was harder than anticipated. Soot broke into fine particles as it filtered through the fur and settled onto the large surface area represented by hair shafts. Soot was particularly attracted to and held by the natural oils of the hair, and to oily sprays that had been used by taxidermists to add sheen to specimens. Whereas feather cleaning techniques had endeavoured to lessen disruption of soot agglomerations, fur cleaning would involve intrusive techniques to reach all hair surfaces.

Vacuuming with a conventional crevice tool and with the vacuum wand (without the nylon screen) removed more than 85% of soot from short-haired mammals. By contrast, the crevice tool removed only 10% of soot from the longer-haired specimens while the wand removed nothing.

Based on methods noted in the literature and personal experience with soot removal, tests were conducted using dry and wet cleaning materials (5,7). Cleaning tests were performed after the vacuum crevice tool was used. Test patches were made on the back of an arctic fox (long soft white hair) and a weasel (short stiff hair).

A few materials—Groom/stick, Webril, Chemical Sponges, and tac cloth—were used by wiping across the direction of growth, but resulted in little soot removal. Other dry cleaning materials were dusted on, rubbed into the fur, and then vacuumed. Materials used in this way were cornmeal, 13 gauge glass beads, and magnesium carbonate (8). Although cornmeal removed between 50% (fox) and 70% (weasel) of the soot, it was not entirely removed and would be a source for pest infestation. The carbonate powder stuck to the fur along with the soot. Greater than 85% removal of soot was achieved by use of the glass beads on the short-haired weasel; soot was attracted to the large surface area presented by the beads, which rolled easily from the fur.

Because wet cleaning appeared a necessary step in cleaning the long haired animals, wet cleaning tests were conducted on the arctic fox. All cleaners were applied to pre-vacuumed fur, 40 strokes on a Webril pad: 1% Orvus in distilled water/rinse, 1% Orvus in 5% ethanol/rinse, 1% Orvus in 50% ethanol/water rinse, ethanol, trichloroethylene, 1:1 ethanol:trichloroethylene, 1% Vulpex in ethanol/rinse, 2% ammonia/rinse, and commercial mount-cleaning preparations (The Eliminator and Seabrite). Sites were dried with a cool stream of air along the direction of growth.

Ethanol removed approximately 75% of the soot, leaving a pleasant soft hair, but no soot deposit on the pad (soot may have wicked with the ethanol down the hair shaft). Aqueous solutions were disappointing, at about 20% removal, except for ammonia which removed 50%, but left a yellowed fur. Trichloroethylene removed 85% of soot, but left the fur quite dried. The commercial mount cleaners left the fur extremely clean, but unacceptably dry and frizzy.

The technique used for removal of heavy soot from short-haired mammals was vacuuming with a crevice tool, followed by application of 13 gauge glass beads. Straight vacuuming with a crevice tool and then wet cleaning with either ethanol or trichloroethylene were the most successful alternatives for the animals with longer hair. All cleaning materials and methods were used and combined, depending upon the degree of soot deposition and character of the fur.



### Conclusion

Post-fire cleanup of a natural history collection can involve the added complication of cleanup within a building that is itself being cleaned and refurbished. Careful organization and documentation is essential.

Soot removal from a wide variety of surfaces was accomplished through use of a progressive cleaning technique involving vacuum suction, followed by dry and, sometimes, wet cleaners. Some cleaning products lent themselves well to soot removal through lifting minute particles with minimal breakup, dispersion, and extraction. Dry cleaning materials used with success were those that mechanically lifted and held soot; wet solutions were primarily aqueous. Cleaning of soot-covered feathers was done with a specially designed vacuum wand, Webril, Groom/stick, and 1% Vulpex in a trichloroethylene/rinse. Cleaning of soot-dusted feathers was performed with particular use of an owl wing and Webril. Soot removal from mammals was accomplished with use of a vacuum crevice tool followed by cleaning with ethanol or trichloroethylene.

### Acknowledgements

Gratitude is expressed to Museum Director Ron Borden, for his willingness to disseminate this information. Our thanks go out to all those who participated in the cleanup of the Saskatchewan Museum of Natural History.

### Materials

Chemical Sponge (vulcanized cis-1,4-polyisoprene, calcium carbonate filler). The Wallmaster brand is distributed by John A. Earl Inc., Hackensack, New Jersey, USA.

Groom/stick (cis-1,4-polyisoprene). Picreator Enterprises Ltd., 44 Park View Gardens, London, England NW4 2PN.

The Eliminator (nonylphenyl ethylene oxide, sodium bicarbonate, silicate). Warrick Co., Indiana, USA.

Orvus liquid (ammonium lauryl sulfate). Distributed by Conservation Materials Ltd, P.O. Box 2884, Sparks, NV, USA 89431.

Scum-X (Dietzgen). Distributed by Talas, 213 West 35th Street, New York, NY, USA 10001-1996.

Seabrite (content unknown). Seabrite Inc., P.O. Box 2368, St. Louis, Mo, USA 63121.

Vulpex (potassium methyl cyclohexyloleate). Distributed by Conservation Materials Ltd.

Webril. Veratech, 6 Curity Avenue, Toronto, Ontario, Canada, M4B 1X2.

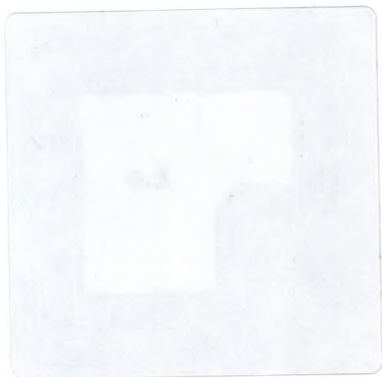
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